Yale Bicentennial Publications

STUDIES

FROM THE

CHEMICAL LABORATORY OF THE SHEFFIELD SCIENTIFIC SCHOOL

Yale Bicentennial Publications

With the approval of the President and Fellows of Yale University, a series of volumes has been prepared by a number of the Professors and Instructors, to be issued in connection with the Bicentennial Anniversary, as a partial indication of the character of the studies in which the University teachers are engaged.

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STUDIES

FROM THE

CHEMICAL LABORATORY

OF THE

SHEFFIELD SCIENTIFIC SCHOOL

EDITED BY

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VOLUME II.

NEW YORK: CHARLES SCRIBNER'S SONS
LONDON: EDWARD ARNOLD
1901

Published, October, 1901

UNIVERSITY PRESS · JOHN WILSON
AND SON · CAMBRIDGE, U. S. A.

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PAPERS ON

ORGANIC CHEMISTRY

ON SILVER FORMANILIDE.*

BY W. J. COMSTOCK AND FELIX KLEEBERG.

THAT acid analides can form salts with metals was first shown by Hofmann † in 1865, when he succeeded in preparing the sodium salt of formanilide. Salts of acid amides with the heavy metals had been prepared previously, and since that time numerous investigators have had occasion to work with similar compounds. Bunge ‡ first prepared sodium acetanilide by acting with metallic sodium on the hot solution of acetanilide in xylene, and in the same paper states that he was unable to prepare silver salts of either form, or acetanilide. Hepp's well-known synthesis of mono-methyl aniline from sodium acetanilide shows that the structure of this salt is

$$C_6H_5N < \begin{matrix} Na \\ COCH_3 \end{matrix}$$

Although Tobias § was unable to obtain methyl formanilide from sodium formanilide, it has since been shown by Norton and Livermore, ‖ as well as by Pictet and Crépieux,¶ that this synthesis is possible, so that in this latter salt as well sodium is united with the nitrogen. In the group of analogous thioanilides, which differ from the ordinary acid anilides in that they are readily soluble in cold dilute alkalies, another structure must be assumed for the sodium salts. Wallach ** showed that the sodium salt of thiacetanilide does not give the normal ethyl-thiacetanilide, $C_6H_5N < \begin{matrix} C_2H_5 \\ CSCH_3 \end{matrix}$, by treatment with ethyl bromide, but that an isomeric compound, $C_6H_5N{=}C < \begin{matrix} SC_2H_5 \\ CH_3 \end{matrix}$,

* Amer. Chem. Jour., xii, No. 7.

† Berl. Akad. Ber., 1865, 659.

‡ Ann. Chem. (Liebig), Suppl. vii, 122.

§ Ber. d. chem. Ges., xv, 2452.

‖ Ibid., xx, 2273.

¶ Ibid., xxi, 1106.

** Ibid., xi, 1590.

which he called ethyl-iso-thiacetanilide, is formed. Since then the investigation of similar thio-anilides has led to the conclusion that in the sodium salts of bodies of this class the metal is united with sulphur rather than with nitrogen.

Notwithstanding the failure of Bunge to obtain a silver salt of formanilide, it can be prepared in quantity with no more inconvenience than attends the preparation of other amorphous silver salts that are sensitive to light.

An investigation of this salt has led us to the interesting result that, although in sodium formanilide the metal is, as mentioned above, united with nitrogen, to the silver salt must be assigned the structure $C_6H_5N : C<^{OAg}_{H}$. If silver formanilide and methyl iodide are allowed to react in molecular proportions, silver iodide is formed together with a compound, the analysis of which gave results agreeing with formyl-mono-methyl-aniline, but whose properties and decompositions are entirely different. The boiling-point and the characteristic odor show at once that the body is not formyl-mono-methyl-aniline. With aniline the new compound reacts according to the equation

$$C_8H_9NO + C_6H_5NH_2 = C_{13}H_{12}N_2 + CH_3OH,$$

and the compound, $C_{13}H_{12}N_2$, is the well-known diphenyl-formamidine,

$$CH\begin{matrix}\diagup NHC_6H_5 \\ \diagdown\!\!\diagdown NC_6H_5\end{matrix},$$

the structure of which can be regarded as settled. This reaction and the formation of the new compound from silver formanilide show beyond doubt that its structure is

$$C_6H_5N{=}C<^{OCH_3}_{H};$$

we shall speak of it hereafter as methyl-iso-formanilide, in conformity with the nomenclature adopted by Wallach for the corresponding thio-compounds, or as phenyl-formimido-methyl ether, on account of its analogy to the imido-ethers of Pinner. Below are given the details of the reaction. It is our intention

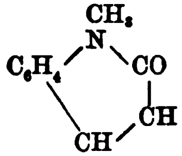
to give a more complete study of this class of compounds at a future date, the object of this paper being to call attention to the behavior of silver formanilide, and the connection of our results with the question of the constitution of compounds containing the group $\underset{|}{\mathrm{N}}\mathrm{H{-}}\underset{|}{\mathrm{C}}\mathrm{O}$ or $\underset{|}{\mathrm{N}}\mathrm{{=}}\underset{|}{\mathrm{C}}\mathrm{.OH}$.

Compounds of this nature received a great deal of attention during the few years succeeding the publication by Baeyer and Oekonomedes * of their work on isatine. Essentially the same question had previously come up regarding cyanic and cyanuric acids, and the method of attacking the problem was the same, *i. e.* to study the ethers. If the ether contained the alkyl group attached to oxygen, it was regarded as proof that the original compound contained the group $\underset{|}{\mathrm{N}}\mathrm{{=}}\underset{|}{\mathrm{C}}\mathrm{.OH}$, while the other arrangement of atoms (now frequently spoken of as the tautomeric form) was assumed when the ether contained the alkyl attached to nitrogen. This led to the adoption of formulæ containing the two different groups for compounds in which the same arrangement might well have been expected. For example, isatine was a lactim having the group $\underset{|}{\mathrm{N}}\mathrm{{=}}\underset{|}{\mathrm{C}}\mathrm{OH}$, and oxindol was a lactam with the group $\mathrm{H}\underset{|}{\mathrm{N}}\mathrm{{-}}\underset{|}{\mathrm{C}}\mathrm{O}$; carbostyril was a lactim, while oxypyridine and hydrocarbostyril were lactams. In preparing the ethers the silver salts were sometimes used; frequently the alkyl halide was made to act on the sodium or potassium salt in alcoholic solution. It was supposed that the result would be the same whichever of these two methods was used. Friedländer,† in collaboration with Weinberg and afterwards with Müller, showed that, according to the method adopted, the lactam-ether (Fig. I) or the lactim-ether (Fig. II) could be prepared from carbostyril.

* Ber. d. chem. Ges., xv, 2093.

† Ibid., xviii, 1528, and xx, 2009.

I.



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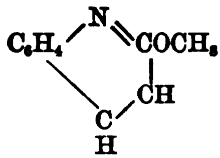
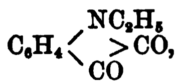


Friedländer suggested that other compounds may show a similar behavior. In looking over the literature up to that date, it is interesting and suggestive to see how the conclusions as to the structure of these compounds depended entirely on the method used in preparing the ethers. Isatine*, isatoxime,† and carbostyril were lactims; their ethers were prepared from the silver salts. γ-Oxyquinaldine,‡ oxynicotinic acid,§ pseudo-lutidostyril,|| and oxindol¶ all gave ethers in which the alkyl group was joined to nitrogen; their ethers were prepared by the action of the alkyl halide and sodium alcoholate or an alcoholic solution of potassium hydroxide. It is especially interesting that ethyl-pseudoisatine-α-ethoxim,** from which Baeyer made ethyl-pseudoisatine,



was prepared with sodium alcoholate and ethyl iodide.

In this connection an experiment which we recently made is worth mentioning, though only indirectly bearing on the rest of this paper. Isatine was boiled in alcoholic solution with ethyl iodide and the theoretical quantity of sodium alcoholate for two hours. On boiling off the greater part of the alcohol and adding water, a dark resinous product separated; this product gave, after shaking out with ether and evaporating the ether, a well-crystallized body, but mixed

* Baeyer and Oekonomedes, Ber. d. chem. Ges., xv, 2093.
† Baeyer and Comstock, Ibid., xvi, 1704.
‡ Knorr and Antrick, Ibid., xvii, 2870.
§ v. Pechmann, Ibid., xviii, 317, and xvii, 2390.
|| Hantzsch, Ibid., xvii, 2903.
¶ Ibid., xvi, 1704.
** Baeyer, Ibid., xvi, 2188.

with a considerable quantity of the resinous material. It was, however, easily purified by crystallizing from boiling water. After a second recrystallization it fused at 95°. The compound corresponds exactly to the description of ethyl-pseudo-isatine. It dissolves in dilute potassium hydroxide giving a light yellow solution, from which it is precipitated at once unaltered on the addition of an acid. The compound,

$$C_6H_4{<}\begin{matrix}N\\CO\end{matrix}{\gg}COC_2H_5,$$

corresponding to the methyl ether obtained by Baeyer and Oekonomedes from the silver salt of isatine, should regenerate isatine under these conditions. We have no intention of entering into a discussion of the "tautomerism" of the groups CO—NH, HO.C=N, but would call attention to the fact that it is the tendency of a silver atom entering into such a compound to give it the form C.OH=N, even where the alkali salts are derived from the lactam form CO—NH.

One compound in which the group CO—NAg has been hitherto regarded as existing beyond question, has interested us on account of the iodine compound made from it: silver succinimide. We shall describe later on the action of iodine on silver formanilide, and the formation of the compound C_7H_6NOI, whose only analogue known thus far (at least as far as its formation is concerned) seems to be Bunge's* "iodo-succinimide," prepared by acting with iodine on silver succinimide. The formation of the compound C_7H_6NOI at ordinary temperature from silver formanilide makes it probable that the compound has the structure $C_6H_5N{=}C{<}\begin{matrix}H\\OI\end{matrix}$. The formation of iodo-succinimide under the same conditions led us to the idea that both iodo- and silver succinimide might be derivatives of the form

$$\begin{matrix}CH_2CO\diagdown\\ |\qquad\quad\ \ N.\\ CH_2C.OH\diagup\!\!\diagup\end{matrix}$$

* Ann. Chem. (Liebig), Suppl. vii, 119.

The experimental verification of this did not, however, work as smoothly as we had hoped. The results will be published at a later date.

Silver Formanilide. — This salt can be prepared by dissolving the sodium salt in alcohol of about 50 per cent, and gradually adding the theoretical quantity of silver nitrate, also in dilute alcoholic solution, stirring the solution well meanwhile. After the silver nitrate solution is all added it is advantageous to add more water and wash partly by decantation. The salt is white when first precipitated, but by the time it has been washed and dried it always has a gray color, light or dark according to the time used and its exposure to light. It is amorphous. A quicker method of preparing it is to dissolve the theoretical quantities of formanilide and silver nitrate in dilute alcohol, adding gradually the theoretical quantity of pure sodium hydroxide with constant stirring, and washing with water as in the other method. At ordinary temperature the salt is quite stable. Unless great care is used to avoid an excess of the alkali and to use pure alkali, the purity of the salt suffers.

A silver determination gave Ag = 47.89 per cent; calculated for $C_6H_5{=}NC{<}^{OAg}_{H}$, Ag = 47.37 per cent.

Methyl-iso-formanilide. — When silver formanilide is treated with methyl iodide in molecular proportion, the iodide being diluted with a small quantity of perfectly dry ether, a thick paste is formed, or indeed, where the quantity of ether used is small, the liquid is entirely absorbed by a part of the salt while the rest looks perfectly dry. On standing for a time at ordinary temperature the appearance of the mixture gradually changes; it becomes more fluid, and after 24 hours the formation of silver iodide seems to be complete. When large quantities are used the reaction is accompanied by evolution of heat, sufficient to make the ether boil. More ether is now added and the liquid filtered from silver iodide. After boiling off the ether a heavy oil is obtained, the greater part of which boils from 195°–200°, and on redistilling, a colorless product, boiling at 196°–198°, results.

Analysis showed the composition C_8H_9NO.

	Calculated for C_8H_9NO.	Found.
C	71.11	71.39
H	6.66	6.89
N	10.37	10.41

As to the structure of this compound there can be no question; it is represented by the formula

$$C_6H_5N{=}C{<}{}^{H}_{OCH_3}.$$

The tendency of methyl-iso-formanilide to form diphenyl formamidine is marked; it is analogous to the behavior of the imido-ethers and the iso-thio-anilides. When mixed with aniline in molecular proportions, the mixture warms up and finally becomes solid. The amidine was purified by recrystallization from alcohol.

The reaction is

$$C_6H_5N{=}C{<}{}^{H}_{OCH_3} + C_6H_5NH_2 = C_6H_5N{=}C{<}{}^{H}_{NHC_6H_5} + CH_3OH.$$

The same reaction takes place when aniline is added to methyl-iso-formanilide in the presence of a large quantity of water. A dilute solution of aniline hydrochloride converts it at once into the hydrochloric acid salt of diphenyl-formamidine. For the preparation of the amidine the addition of aniline is not necessary. If hydrochloric acid, strong or dilute, is added to methyl-iso-formanilide, diphenyl-formamidine hydrochloride is formed at once. This is easily understood in the light of the former reactions. The reaction takes place in two phases. The first change is represented by the equation,

$$C_6H_5N{=}C{<}{}^{OCH_3}_{H} + H_2O + HCl = C_6H_5NH_2HCl + HCOOCH_3;$$

and, second, the aniline hydrochloride formed acts at once on unaltered methyl-iso-formanilide. In the first phase the reaction is exactly analogous to the behavior of benzylidene-aniline, $C_6H_5CH{=}NC_6H_5$, on treatment with acids. The formation

of the amidine also takes place, though slowly, on exposing the iso-formanilide to moist air. In all cases the diphenyl-formamidine melted at 137°–138° after recrystallizing from alcohol.

	Calculated for $C_{13}H_{12}N_2$.	Found.
C	79.60	79.82
H	6.12	6.15
N	14.28	13.94

Analysis, a comparison of the compound with diphenyl-formamidine prepared by other methods, and the splitting off of aniline * by boiling with dilute alcohol, serve to establish the identity of the compound beyond question.

Action of Iodine on Silver Formanilide. — When the finely pulverized silver salt is mixed with dry chloroform and one molecule iodine is added, the formation of silver iodide begins at once. If the iodine is dissolved in chloroform before it is added, the reaction takes place rapidly at ordinary temperature; but no harm is done by warming on the water-bath. In taking molecule for molecule of the silver salt and iodine, the chloroform solution retains the iodine color, but on adding an excess of silver salt it is colored amber-yellow. After filtering from the silver iodide the solution is concentrated, first on the water-bath, finally at ordinary temperature, by passing a current of dry air over it until quite a quantity of light yellow crystals has separated. These are washed with dry ether to free them from the mother-liquor and from a small quantity of reddish oil. The new compound can be recrystallized from ether or chloroform, but unless great care is taken to work quickly and avoid moisture there is a separation of iodine. Dry ether or pure acetone can be used in place of chloroform in making the reaction, but we obtained a better yield in using chloroform and working with small quantities. The best yield was 2.7 g. from 5 g. silver salt. On heating the compound decomposes with separation of iodine; the separation is less, the more slowly it is heated. After

* Ber. d. chem. Ges., xv, 2450.

keeping for a time it also smells strongly of iodine, and iodine crystals can be observed. An iodine estimation gave 50.27 per cent iodine. The theory for C_7H_6NOI requires 51.42 per cent iodine. The iodine determination shows clearly that the compound is derived from silver formanilide, by the introduction of one atom of iodine in the place of silver. Bunge has shown that iodine does not react with sodium formanilide, in which the metal is united with nitrogen.

We have shown that in silver formanilide the metal is attached to oxygen. The ready formation of the new compound from silver formanilide at ordinary temperature, together with Bunge's observation, seem to warrant our conclusion that its structure is represented by the formula

$$C_6H_5N{=}C{<}\substack{H\\OI}.$$

Perhaps the best name that can be given to it is iodo-iso-formanilide. Iodo-iso-formanilide is decomposed by water, but we have not attempted to study the products. No definite melting-point can be given. When slowly heated the separation of iodine is not large, and the contents of the tube are melted at about 110°, but in this case a second compound, the result of molecular rearrangement, is formed.

Para-iodo-formanilide. — After heating iodo-iso-formanilide slowly and keeping the temperature for a few minutes at 115°, then crystallizing from water, we obtained this second body in fine white transparent needles melting at 109°–110°. An iodine estimation gave 51.13 per cent iodine.

The theory for C_7H_6NOI requires 51.42 per cent. This same rearrangement can be effected by heating iodo-iso-formanilide for a few minutes with formic acid; indeed, on adding formic acid it dissolves, heat is evolved, and the new compound needs only to be crystallized from water. The new body is para-iodo-formanilide. To prove its identity we prepared para-iodo-aniline by the method described by Michael and Norton,* and made the formyl compound. By boiling *p*-iodo-aniline with a slight excess of formic acid for a

* Ber. d. chem. Ges., xi, 108.

few minutes, boiling off the excess of acid and crystallizing from hot water, we obtained the formyl compound in long needles exactly like those obtained from iodo-iso-formanilide.

	Calculated for $C_6H_4I.NHCHO$.	Found.
Iodine	51.42	51.77

It dissolves easily in alcohol, methyl alcohol, acetone, ether, chloroform and benzene, with difficulty in cold water, more readily in hot water. The melting-point remained constant after repeated recrystallizations from water at 108°–109°.

This formation of para-iodo-formanilide from iodo-iso-formanilide suggests the reaction which Bender described.* From a compound whose structure Bender considered to be

$$C_6H_5N{<}^{Cl}_{COCH_3},$$

he obtained by molecular rearrangement *p*-chlor-acetanilide.

Our conclusion as to the structure of iodo-iso-formanilide suggested a re-examination of a number of compounds in which it has been supposed that the halogen is united to nitrogen. The work is now under way in this laboratory, and the results will be communicated later.

Formation of Carbanilide. — On dry distillation of silver formanilide a solid crystallized compound is formed. This is easily separated from the oily products by washing with alcohol, and can be obtained pure by recrystallizing from alcohol. It turned out to be *s*-diphenyl-urea.

	Calculated for $CO(NHC_6H_5)_2$.	Found.
C	73.59	73.32
H	5.66	6.00
N	13.20	13.43

It fused at 231°–233°, corresponding exactly to a specimen of diphenyl-urea prepared according to Weith.† We also converted some of the diphenyl-urea, obtained from silver forman-

* Ber. d. chem. Ges., xix, 2273. † Ibid., ix, 821.

ilide, into triphenyl-guanidine, which melted at 144°, so that its identity is certain. The reaction by which it is formed can be formulated:

$$2C_6H_5N{=}C{<}{}^{H}_{OAg} = 2Ag + CO + CO{<}{}^{NHC_6H_5}_{NHC_6H_5}.$$

That carbon monoxide is formed we proved in the customary way. The formation of disubstituted ureas from silver salts of the formyl compounds seems to be general. On distilling silver form-para-toluide, and recrystallizing the product from alcohol, we obtained dipara-tolyl-urea melting at 255°.

	Calculated for $CO{<}{}^{NHC_6H_4CH_3}_{NHC_6H_4CH_3}$	Found.
C	75.00	74.77
H	6.67	6.77
N	11.66	11.63

SHEFFIELD LABORATORY, NEW HAVEN.

RESEARCHES ON THE ISO-ANILIDES.*

By W. J. COMSTOCK and H. L. WHEELER.

In the first part of this paper we shall describe experiments which show that the sodium and silver salts of form-α-naphthalide and of metanitro-formanilide show, in their behavior towards methyl iodide, the same difference that has been found in the salts of other aromatic formyl compounds. The second part contains a description of experiments made with the iso-anilides, showing that they react with secondary amines, both fatty and aromatic, and with cyan-amide.

Gattermann † made the interesting observation that nitro-para-acetoluide occurs in two modifications, and suggested the possibility that these two modifications might correspond to the forms containing the two groups —N=C(OH)— and —NH—CO—. It seemed possible that in the case of nitro-formanilide — whose salts behave towards methyl iodide as if they had the structures —NNa—CO— and —N=C(OAg) respectively — these two modifications might be obtained by decomposing the salts. But we were able to obtain but a single modification of the metanitro-formanilide in this way. The decomposition of both salts by dry hydrochloric acid in presence of dry ether and in presence of dry chloroform; the decomposition of the silver salt by dry hydrogen sulphide in presence of dry ether; and the decomposition of the sodium salt by moist carbonic acid in presence of ether, — all gave products having the same melting-point. In each case, on evaporating the solution at ordinary temperature, the crystals had exactly the same appearance under the microscope, consisting of tufts of extremely fine, hair-like, bent needles. Under these condi-

* Amer. Chem. Jour., xiii, No. 8.   † Ber. d. chem. Ges., xxiii, 1733.

tions we could not, however, obtain crystals that were fitted for crystallographical or optical examination.

Silver Salt of Form-α-naphthalide.—Prepared by adding gradually the theoretical quantity of silver nitrate in 50 per cent alcoholic solution to the aqueous alcoholic solution of sodium hydroxide and the formyl compound. The silver salt separates as a voluminous gray precipitate, amorphous and sensitive to light, insoluble in water.

	Found.	Calculated.
Ag	39.14	38.84

Methyl-iso-Form-α-naphthalide. — Prepared by treating the dry silver salt with methyl iodide in presence of dry ether, this compound is obtained as a heavy oil, having a strongly fishy odor, and boiling at ordinary pressure, with noticeable decomposition at 306°–308°.

	Found.	Calculated.
C	77.8	77.7
H	5.9	6.0

It shows the same behavior towards water, dilute acids, and primary amines that methyl-iso-formanilide does.

Di-α-naphthyl-formamidine. — Formed by treating the above-described ether with α-naphthylamine, and recrystallizing from hot benzene. It forms colorless plates, which melt at 199°, and are moderately soluble in alcohol, ether, and benzene, insoluble in ligroin. Does not dissolve in cold, dilute mineral acids.

	Found.	Calculated.
C	85.2	85.1
H	5.5	5.4
N	9.4	9.5

Phenyl-α-naphthyl-formamidine, prepared by treating methyl-iso-form-α-naphthalide with aniline, is purified by dissolving in benzene and precipitating with ligroïn. Its melting-point is 142°. It is soluble in alcohol, ether, and benzene, difficultly soluble in ligroïn.

	Found.	Calculated.
C	83.3	82.9
H	5.8	5.7
N	11.3	11.4

The basic properties are much more strongly marked than in the case of the dinaphthyl-amidine.

The reaction of methyl iodide with the sodium salt of form-*a*-naphthalide is not a satisfactory operation, owing to the properties of the methyl-naphthyl-amine. However, by Hepp's method, we obtained the base corresponding to that described by Landshoff.* An attempt to purify it by means of the nitrosamine was a failure, as nitrous acid seemed to have a more complicated action, and left a most uninteresting resinous product. However, by means of the acetyl compound described by Landshoff, we were able to identify the secondary amine.

Meta-nitro-formanilide. — This is easily prepared by boiling meta-nitraniline with an excess of pure formic acid, adding water and recrystallizing from hot water, alcohol, or benzene. It melts at 134°. It is soluble in hot water, alcohol, and benzene; difficultly soluble in ether and ligroin.

	Found.	Calculated.
C	50.6	50.6
H	3.9	3.6

Sodium Meta-nitro-formanilide. — To prepare the sodium salt, the best method is to dissolve the theoretical quantity of sodium in the smallest possible quantity of pure, dry methyl alcohol, and add it to the formyl body, which has been moistened to a paste with methyl alcohol. The lemon-yellow salt which is formed is readily soluble in methyl alcohol, and should be washed thoroughly with dry ether. A sodium estimation in the salt thus prepared gave Na = 12.1 per cent (calculated, Na = 12.2 per cent). Exposed to the air, the salt gradually absorbs carbonic acid, and is finally completely converted into sodium carbonate and the formyl compound. If

* Ber. d. chem. Ges., xi, 638.

in preparing the sodium salt the methyl alcohol is not thoroughly washed out by ether, the lemon-yellow salt gradually changes into a mass of orange-colored needles, which, dried over sulphuric acid, gave Na = 10.1 per cent. The theoretical percentage for the sodium salt with 1 molecule of CH_3OH is Na = 10.45. The same orange-colored needles are obtained when the alcoholic solution is concentrated. On adding water to the alcoholic solution of the salt, the free formyl compound is precipitated.

Action of Methyl Iodide on the Sodium Salt. — Methyl iodide reacts but slowly with the sodium salt when warmed on the water-bath in a flask fitted with an inverted condenser; nevertheless the reaction can be made to take place in this way if the heating be continued for some days, care being taken to exclude moisture and carbonic acid.

The reaction is finished when a specimen of the mixture no longer shows an alkaline reaction. The reaction takes place in a very few hours when conducted in a sealed tube at 100°. In either case, by crystallizing from alcohol, the nitro-formyl-methyl-aniline can be obtained in long needles, having a slight yellowish tinge and melting at 70°–71°.

	Found.	Calculated.
C	53.0	53.3
H	4.5	4.4

The meta-nitro-monomethyl-aniline prepared from the pure formyl compound melted at 67°, and the nitrosamine, which we obtained perfectly white, melted at 76°. Nölting and Stricker * gave 65°–66° and 68°–70° as the melting-points of these two compounds.

Silver Meta-nitro-formanilide. — The silver salt can be prepared in aqueous-alcoholic solution in the same manner as silver formanilide. It is amorphous, and, when first precipitated, colorless. It can be washed with hot water.

	Found.	Calculated.
Ag	39.8	39.3

* Ber. d. chem. Ges., xix, 548.

Meta-nitro-methyl-iso-formanilide is prepared by treating the dry silver salt with methyl iodide diluted with ether. On fractioning at a pressure of 21 mm., the iso-anilide was obtained, boiling at 172°–173°; temperature of bath, 190°. The compound solidifies in the receiver to a mass of long, slender, light-yellow needles, melting at 45°.

	Found.	Calculated.
C	53.5	53.3
H	4.5	4.4
N	15.8	15.6

The ether reacts with primary amines, as do the others thus far described, but the tendency to form the amidine in presence of water is not so marked as in the case of the non-substituted iso-anilides. Treated with dilute hydrochloric acid, for instance, the salt of meta-nitraniline is obtained at once.

Dinitro-diphenyl-formamidine, $CH\begin{matrix}\diagup\!\!\diagup N.C_6H_4.NO_2 \\ \diagdown NH.C_6H_4.NO_2\end{matrix}$.—A mixture of the theoretical quantities of the iso-anilide and meta-nitraniline, heated up slowly on a bath, remained liquid from 50° to about 110°, at which temperature the mass became solid. On recrystallizing from alcohol, the amidine was obtained in small yellow hair-like needles, melting at 195°–196°. A combustion of the substance dried at 130° gave the following results:

	Found.	Calculated.
C	54.9	54.5
H	3.6	3.5

The compound is soluble in alcohol, ether, chloroform, and acetone; insoluble in ligroin.

Mono-nitro-diphenyl-formamidine, $CH\begin{matrix}\diagup\!\!\diagup N.C_6H_4.NO_2 \\ \diagdown NH.C_6H_5\end{matrix}$. On adding the theoretical quantity of aniline to the fused ether, the mixture solidifies in a few minutes, and when crystallized from absolute alcohol the amidine is obtained in long yellow prisms which melted at 145°.

	Found.	Calculated.
C	64.8	64.7
H	4.7	4.6

The following experiments will serve to show that the iso-anilides react with secondary amines, fatty and aromatic, forming tri-substituted amidines:

Diethyl-phenyl-formamidine, $CH\begin{smallmatrix}/\!\!/ N.C_6H_5 \\ \diagdown N.(C_2H_5)_2\end{smallmatrix}$.—A mixture of methyl-iso-formanilide and a slight excess of diethyl-amine was boiled in a flask fitted with an inverted condenser for about two hours, and then distilled at ordinary pressure. Practically the entire quantity came over between 265° and 275°. On redistilling, a nearly colorless oil was obtained, boiling at 273°–275°. There was, however, a noticeable decomposition, and the compound had a strongly alkaline odor. Converted into the gold double-salt and recovered, the amidine is colorless and odorless. The gold double-salt is difficultly soluble in water, easily soluble in alcohol, and crystallizes in small lemon-yellow plates when water is added to the alcoholic solution; the plates melt at 147°. After drying over sulphuric acid *in vacuo*, its analysis gave the following results:

	Found.	Calculated for $CH\begin{smallmatrix}/\!\!/ N.C_6H_5 \\ \diagdown N.(C_2H_5)_2\end{smallmatrix}.HCl + AuCl_3$.
C	25.9	25.6
H	3.5	3.3
N	5.4	5.4
Au(=196.6) .	37.9	38.1

Methyl-diphenyl-formamidine, $CH\begin{smallmatrix}/\!\!/ N.C_6H_5 \\ \diagdown N<\begin{smallmatrix}CH_3 \\ C_6H_5\end{smallmatrix}\end{smallmatrix}$. — A mixture of monomethyl-aniline and methyl-iso-formanilide was allowed to stand at ordinary temperature for some days, and, after having been warmed on the water-bath a short time, was distilled under diminished pressure: an excellent yield of the amidine was obtained. The substance is a heavy yellowish

oil, boiling at 214° under 22 mm. pressure; temperature of bath, 260°.

	Found.	Calculated.
C	79.6	80.0
H	6.7	6.7
N	13.5	13.3

The gold double-salt is difficultly soluble in water, and when water is added to the alcoholic solution crystallizes in gold-colored plates which melt at 145°. A gold estimation in the air-dried salt gave Au = 35.7 per cent; calculated for the anhydrous salt, Au = 35.7 per cent.

Action of Cyan-amide on the Iso-anilides.

Cyan-phenyl-formamidine, $CH\begin{matrix}\diagup\!\!\diagup N.C_6H_5 \\ \diagdown N.H.CN\end{matrix}$. — When an ethereal solution of cyan-amide and methyl-iso-formanilide is allowed to stand at ordinary temperature, it soon begins to deposit a crystalline crust, the separation of which is practically complete in 24 hours, unless the solution is very dilute. The new compound, after washing with ether, can be recrystallized from hot water or alcohol, in both of which it is quite soluble. From alcohol it separates in long, flat, colorless prisms; from hot water, in long needles. Its melting-point is 138°. Its analysis corresponds to the formula $C_8H_7N_3$, and its structure is in all probability represented by the formula

$$CH\begin{matrix}\diagup\!\!\diagup N.C_6H_5 \\ \diagdown N.H.CN\end{matrix}.$$

	Found.	Calculated.
C	66.0	66.2
H	5.0	4.8
N	29.0	29.0

Cyan-para-tolyl-formamidine. — Cyan-amide reacts with methyl-iso-form-para-toluide in ethereal solution in the same way that it does with the iso-anilide. Recrystallized from

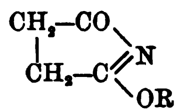
alcohol, the new body is obtained in long, well-developed prisms which melt at 176°–177°.

	Found.	Calculated.
C	68.0	67.9
H	5.7	5.6
N	26.3	26.4

ON THE PREPARATION OF OXYGEN-ETHERS OF SUCCINIMIDE FROM ITS SILVER SALT.*

By W. J. COMSTOCK and H. L. WHEELER.

The action of ethyl iodide on silver succinimide has already been tried by Menschutkin,† as well as by Landsberg, ‡ in the course of his extended investigation on the imides of dibasic acids. Both investigators state that they obtained only silver iodide and regenerated succinimide. Comstock and Kleeberg § found that by treating dry silver succinimide with methyl iodide, at most a trace of succinimide was regenerated; but they did not obtain the resulting compound in a pure state. That it was not the well-known methyl succinimide, *i. e.*, the nitrogen-ether of succinimide, was shown by the fact that it reacted with aniline, with the formation of the base to be described later. We have taken up the work at this point, and succeeded in preparing in a state of purity the ethyl and propyl compounds resulting from the action of the corresponding iodides on silver succinimide. These compounds were found to be isomeric with the nitrogen-ethers of succinimide, and have, without doubt, the structure



We have not attempted to prepare the corresponding methyl-derivative, as its boiling-point was found by Kleeberg to be too near that of the nitrogen-ether to allow a separation by fractional distillation, in case any nitrogen-ether should be formed in the reaction. It is absolutely essential in preparing

* Amer. Chem. Jour., xiii, No. 8.

† Ann. Chem. (Liebig), clxii, 170.

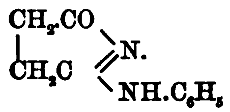
‡ Ibid, ccxv, 211.

§ Ber. d. chem. Ges., xxiii, 2274; Amer. Chem. Jour., xii, 493.

the oxygen-ethers, to exclude all moisture, even after the reaction is over, as the pure bodies form succinimide when exposed to moist air:

$$C_4H_4NO_2R + H_2O = C_4H_5NO_2 + ROH.$$

This ready formation of succinimide from the oxygen-ethers explains Landsberg's failure to obtain anything but silver iodide and succinimide when he allowed ethyl iodide to act on the dry silver salt in presence of dry benzene. We have found that the oxygen-ethers are formed in presence of dry benzene, ether or chloroform, the last being used in conducting the reaction with larger quantities. The formation of the oxygen-ether can readily be detected after filtering from the silver iodide, by evaporating the solvent and adding a few drops of aniline. The base formed has the composition $C_{10}H_{10}N_2O$, and has without doubt the formula



Succinimide is thus placed in the category with formanilide and other formyl compounds of primary aromatic amines, since it was shown by Landsberg that the alkaline salts give the nitrogen-ethers when treated with alkyl iodides. We were also able to show that in each case a small quantity of the nitrogen-ether had been formed from the silver salt. This was done by decomposing the ethers with a solution of potassium hydroxide, and showing the presence of a primary amine by the iso-nitrile reaction. This formation of a small quantity of nitrogen-ether from the silver salt renders the assumption of a different structure for the sodium and silver salts less satisfactory, as in that case refuge must be taken in the assumption of a molecular rearrangement at low temperature. We have attempted to find experimental evidence that might throw more light on this interesting subject, but as our results have been thus far negative, we present the definite experimental results already obtained and postpone the discussion of the theory till a future date.

Oxygen-ethyl Succinimide. — Silver succinimide dried to a constant weight at 100° was allowed to stand for several weeks at ordinary temperature with the theoretical quantity (1 mol.) of ethyl iodide diluted with two to three times its weight of dry chloroform. After filtering off the silver iodide and washing with more dry chloroform, the chloroform was distilled off on the water-bath, and the dark, oily residue distilled under diminished pressure. A second distillation yielded the oxygen-ether as a colorless oil, boiling at 144°–146° under a pressure of 20 mm., the temperature of the bath being 190°. The compound decomposes when boiled at ordinary pressure, and even at 20 mm. a slight decomposition can be noticed. Analysis gave results agreeing with the theory.

	Found.	Calculated for $C_6H_9NO_2$.
C	56.62	56.69
H	7.11	7.09

On adding aniline the mixture solidifies at once, and with noticeable evolution of heat if more than a few drops are used in the reaction. When exposed to moist air the pure ether gradually solidifies, forming succinimide, which shows the correct melting-point without recrystallization. In order to test for the presence of the nitrogen-ether, a small quantity of the chloroform solution, representing about six to eight g. of silver salt freshly filtered from silver iodide, was treated with water and allowed to stand several hours after vigorous shaking. The chloroform was then distilled off, the aqueous solution distilled with potassium hydroxide, and an examination for primary amine made in the way described under the propyl-ether. The presence of a primary amine was shown beyond doubt, therefore some nitrogen-ether had been formed in the reaction. If the nitrogen-ether is formed by molecular rearrangement from the oxygen-ether, that rearrangement must take place in this case at ordinary temperature, as the oxygen-ether must have been completely converted into succinimide by the action of the water before

any heat was applied. The nitrogen-ethyl-ether, which was prepared for comparison according to Menschutkin, boiled at 235° at 763 mm. pressure (Menschutkin gives 234°), and at 20 mm. showed the boiling-point 122°; temperature of bath, 155°. It does not react with aniline.

Oxygen-propyl-succinimide. — This was prepared in the same way as the corresponding ethyl compound, but the reaction took place more slowly. After five weeks the chloroform solution was filtered from the iodide, and it was found that a noticeable quantity of silver iodide separated on evaporating the solution, so that the residue was again taken up in chloroform and treated as described under the ethyl-ether. At the first distillation it was found that at 19 mm. pressure but a few drops came over below 153°, while almost the entire quantity boiled between 153° and 160°. On redistilling, the greater part came over at 153°–154° (pressure, 19 mm.; temperature of bath, 195°), again leaving a dark residue.

Analysis gave the following results:

	Found.	Calculated for $C_7H_{11}NO_2$.
C	59.10	59.57
H	7.95	7.80
N	10.30	9.92

The slight variation of our results from the theory would indicate the presence of a small quantity of succinimide, but as its boiling-point must be very close to that of the ether, a separation would hardly be possible, and is indeed not necessary. Like the corresponding ethyl-ether, it decomposes when boiled at ordinary pressure; gives succinimide when exposed to the air, and reacts at once with aniline. As the nitrogen-propyl-ether has a lower boiling-point than the oxygen-ether, the first portions of the distillate from the impure oxygen-ether were examined for the nitrogen-ether. It was impossible, from the boiling-points given, that more than a small quantity of nitrogen-ether could be present, and this could hardly be separated in a pure state. So the first portions of the distillate were boiled with a strong solution of potassium hydrox-

ide as long as any volatile base came off, the volatile part being caught in dilute hydrochloric acid. On evaporating the acid solution it was found from its insolubility in cold absolute alcohol, that the greater part of the residue consisted of ammonium chloride, but that in that portion soluble in alcohol we could positively identify propyl-amine by the iso-nitrile reaction. Therefore a small quantity of the nitrogen-ether is formed together with the oxygen-ether.

Nitrogen-propyl-succinimide. — For comparison we prepared this compound by the same method that Menschutkin used in making the methyl- and ethyl-compounds — by distilling the acid succinate of propyl-amine. We obtained it as a colorless oil boiling at 247°–248° at 763 mm. pressure. When cooled in a freezing-mixture it solidifies and shows the melting-point 15°–16°. It boiled at 136°–137° at 27 mm. pressure. It does not form the base $C_{10}H_{10}N_2O$ with aniline. A nitrogen estimation gave N 9.92 per cent; the theory requires 9.80 per cent.

Base $C_{10}H_{10}N_2O$. — This base is formed at once, as we have before stated, on adding aniline to one of the oxygen-ethers of succinimide. If the ether be pure, the resulting base needs only to be recrystallized from alcohol. If an impure ether be used, the base can be readily purified by dissolving it in cold dilute hydrochloric acid, filtering from the dark residue and precipitating with ammonia. Its melting-point is 216°. It crystallizes from hot alcohol, on cooling rapidly, in small, transparent quadrilateral plates. Dried at 100°, its analysis gave the following results:

	Found.	Calculated for $C_{10}H_{10}N_2O$.
C	69.36	68.96
H	5.79	5.74
N	16.20	16.09

The gold double-chloride of the base is precipitated from the acid solution on adding gold chloride. When prepared in the cold, the double salt forms a voluminous, sulphur-yellow precipitate consisting of microscopic needles. When the gold-

chloride solution is added to the hot acid solution of the base, the double salt separates on cooling in gold-yellow prisms. The salt should not stand long in contact with the mother-liquor; even when filtered quickly and dried *in vacuo* over sulphuric acid, it turns green on the surface. A gold estimation gave Au = 38.46 per cent; calculated for $C_{10}H_{10}N_2O.HCl.AuCl_3$, Au (= 196.6) = 38.38. The salt melts with decomposition at 170°.

ON SOME DERIVATIVES OF AROMATIC FORMYL COMPOUNDS.*

By W. J. COMSTOCK and R. R. CLAPP.

The curiously different behavior of the sodium and silver salts of formanilide towards methyl iodide, as shown by Comstock and Kleeberg,† is of especial interest as the first case of a compound containing the group

$$—NH—CO— [\text{or } —N{=}C(OH)—],$$

whose sodium salt yields, under conditions which exclude dissociation, the nitrogen-ether, — *i. e.* formyl-monomethyl-aniline, — while the silver salt gives the oxygen-ether — *i. e.*, methyl-iso-formanilide, $C_6H_5N{=}C{<}^{H}_{O.CH_3}$. We have continued the experiments in that direction and found that form-ortho-toluide and form-para-toluide behave in the same way: both give silver salts which, on treatment with methyl iodide, yield iso-toluides; and the sodium salt of each can be used for preparing the secondary amine. As a contribution to our knowledge of the iso-anilides, we have also prepared seven higher ethers and found that they give the same reactions, — formation of diphenyl-form-amidine by the action of aniline, by the action of a dilute acid, and by the gradual absorption of water on exposure to the air. We have also found, though without purifying and analyzing the products, that methyl-iso-formanilide reacts with other primary aromatic amines as well as with aniline; and have prepared and analyzed the amidines formed by treating it with hydroxyl-amine and benzyl-amine. On decomposing the silver salt of form-para-toluide in presence of dry ether with dry hydrochloric acid gas or with dry hydrogen sulphide — care

* Amer. Chem. Jour., xiii, No. 8. † Ibid., xii, 493.

being taken to have the silver salt in excess, — we found, on evaporating the ether at ordinary temperature under diminished pressure, that the residue fused at 52°, as did also a specimen of pure form-para-toluide attached to the same thermometer. Nor could we observe, as the compound crystallized from ether, any difference in crystalline form which could warrant the assumption that an isomer had first been formed and afterwards transformed during the heating into the more stable ordinary form-para-toluide. This suggests the similar behavior of silver benzamide * towards hydrochloric acid and hydrogen sulphide; although with methyl iodide it gives the imido-ether $C_6H_5.C\begin{smallmatrix}\diagup O.CH_3\\ \diagdown\!\!\diagdown NH\end{smallmatrix}$. In the case of benzamide, however, the sodium salt could not be prepared. In form-para-toluide we have therefore a case in which sodium and silver salts regenerate the same mother-substance, while they behave differently towards methyl iodide. As we have been unable to find any experimental proof, either of the existence in the free state of an isomeric form-para-toluide, or that in treating the salts with iodides anything beyond a direct replacement of metal by alkyl occurs, the best explanation seems to be that the salts have a different structure, while only one form of the free formyl compound is capable of existing. Possibly in some of the compounds belonging to this class it will be found that both forms are capable of existing.

Derivatives of Form-ortho-toluide and Form-para-toluide. — The silver salts of both these compounds can be made by exactly the same method as was used in preparing silver formanilide. The preparation of the iso-form-toluides from the silver salts is exactly like the preparation of methyl-iso-formanilide, and they show the characteristic behavior of the latter compound. The two amidines were made from the iso-toluides by the action of the corresponding toluidines.

Silver Form-ortho-toluide is amorphous and sensitive to light; it is insoluble in cold water.

* Tafel and Enoch, Ber. d. chem. Ges., xxiii, 103.

	Found.	Calculated.
Ag	44.37	44.63

Methyl-iso-form-ortho-toluide is an aromatic oil boiling at 211°–213° at 760 mm. pressure.

	Found.	Calculated for $C_9H_{11}NO$.
C	72.42	72.48
H	7.38	7.38
N	9.71	9.39

Di-ortho-tolyl-formamidine, when recrystallized from alcohol, melted at 150°.

	Found.	Calculated for $C_{15}H_{16}N_2$.
C	80.30	80.36
H	7.9	7.14

This compound has already been made by Ladenburg * and by Senier † by other methods.

Silver Form-para-toluide was obtained as a voluminous precipitate consisting entirely of small needles, practically insoluble in cold water; sensitive to light.

	Found.	Calculated.
Ag	44.98	44.63

Methyl-iso-form-para-toluide is an aromatic oil boiling at 216°–218° at 761 mm. pressure.

	Found.	Calculated for $C_9H_{11}NO$.
C	72.44	72.48
H	7.54	7.38
N	9.56	9.39

Di-para-tolyl-formamidine, when purified by crystallization from pure benzene — from which it separates in flat, transparent, colorless prisms of considerable size — melts at 140°.

	Found.	Calculated for $C_{15}H_{16}N_2$.
C	80.45	80.36
H	7.21	7.14
N	12.60	12.50

* Ber. d. chem. Ges., x, 1260.

† Ibid, xviii, 2294.

This amidine was also prepared by Senier.*

In trying the behavior of the sodium salts of both formyl compounds towards methyl iodide, we found that the mono-methyl-toluidines could be prepared either by following Hepp's method for the preparation of monomethyl-aniline, or by using sodium methylate and methyl iodide in presence of dry methyl alcohol. The yield is better when Hepp's method is followed, in which case benzene can be used in place of xylene, although the action of the sodium is then much slower. The secondary base was, however, in no case obtained absolutely pure until converted into the nitroso-compound and recovered. Monomethyl-ortho-toluidine boiled at 280°; the para-compound at 211°–212°.

Ethyl-iso-formanilide is an aromatic oil boiling at 213°–215° at 761 mm. pressure.

	Found.	Calculated for $C_9H_{11}NO$.
C	72.57	72.48
H	7.60	7.38

Propyl-iso-formanilide boils at 233°–235° at 760 mm. pressure.

	Found.	Calculated for $C_{10}H_{13}NO$.
C	73.39	73.62
H	8.24	7.98

Both of these ethers react, as before stated, exactly like the methyl-ether.

Phenyl-benzyl-formamidine.— Benzyl-amine and methyl-iso-formanilide react slowly in the cold when mixed in molecular proportions. The solid crystalline product, after being pressed free from a small quantity of oil, can be recrystallized by dissolving in strong alcohol and adding water until a permanent turbidity results. The base comes down oily at first, but gradually solidifies, forming colorless, transparent, flat prisms, melting at 80°.

	Found.	Calculated for $C_{14}H_{14}N_2$.
C	80.15	80.00
H	6.72	6.66

* Loc. cit.

Action of Hydroxyl-amine on Methyl-iso-formanilide.— On adding methyl-iso-formanilide to an aqueous-alcoholic solution of hydroxyl-amine hydrochloride, a white solid body separates at once. This substance dissolved in dilute alcohol gave on the addition of ammonia a precipitate consisting of small white scales which fused at 130°–131°. From the method of formation the compound is probably phenyl-methenyl-oxamidine of the structure $C_6H_5N=C<^{H}_{NH.OH}$. A combustion gave results agreeing with this formula.

	Found.	Calculated for $C_7H_8N_2O$.
C	61.71	61.76
H	6.17	5.88

Formation of Di-ortho-tolyl-urea.— On distilling dry silver form-ortho-toluide, and recrystallizing the distillate from absolute alcohol, the urea fusing at 247° was obtained.

	Found.	Calculated.
C	74.87	75.00
H	6.68	6.67

ON HALOGEN ADDITION-PRODUCTS OF THE ANILIDES.*

[SECOND PAPER.]

BY H. L. WHEELER AND P. T. WALDEN.

A PRELIMINARY notice was recently given by one of us (Wheeler) on halogen addition-products of the anilides.† In the case of metanitroacetanilide products were prepared which contained bromine in various proportions, but, under certain conditions, the total bromine approximated to that calculated for a dibromine addition-product. These products have now been thoroughly reinvestigated and it has been found that, besides free bromine, they contain hydrobromic acid, and that the products described as dibromine addition-products of metanitroacetanilide were mixtures of the perhalides $(C_6H_4.NO_2.NHCOCH_3)_2HBr.Br_2$ and $(C_6H_4.NO_2.NHCOCH_3)_2HBr.Br_4$.

We have attempted to prepare bromine addition-products of metanitroacetanilide and parabromacetanilide in the absence of hydrobromic acid, but without success. Bromine free from hydrobromic acid can be mixed with these anilides, when suspended in pure carbon bisulphide, without any addition taking place. The unaltered anilides are recovered on filtering and drying. When, on the other hand, bromine containing hydrobromic acid or solvents which are attacked by bromine — such as chloroform, glacial acetic acid, or ligroïn — are used, perhalides are formed.

It has been found in general that when bromine is mixed with an anilide under conditions which permit of the formation of hydrobromic acid, the hydrobromic acid unites with the anilide to form an ammonium salt, *i. e.* $(R.NHCOCH_3)_2HBr$, ‡ and that this salt then adds bromine.

* Amer. Chem. Jour., xviii, No. 2, February, 1896. † Ibid., xvii, 612.

‡ Compare Nölting and Weingärtner, Ber. d. chem. Ges., xviii, 1340; also Roozeboom, Chem. Centrbl., 1886, 498.

We have prepared the salts $[C_6H_4.NO_2.NHCOCH_3]_2HBr$ from metanitroacetanilide; $[C_6H_4.Br.NHCOCH_3]_2HBr$ from parabromacetanilide; and $[C_6H_5.NHCOCH_3]_2HI$ from acetanilide. These salts gave the following series of halogen addition-products:

$(C_6H_4.NO_2.NHCOCH_3)_2HBr.Br_2$
$(C_6H_4.NO_2.NHCOCH_3)_2HBr.Br_4$
$(C_6H_4.NO_2.NHCOCH_3)_2HBr.Br_6$
$(C_6H_4.Br.NHCOCH_3)_2HBr.Br_2$
$(C_6H_4.Br.NHCOCH_3)_2HBr.Br_4$
$(C_6H_5.NHCOCH_3)_2HI.I_2$
$(C_6H_5.NHCOCH_3)_2HI.I_4$

These compounds are perfectly analogous to the perhalides $CsBr.Br_2$,* $CsI.I_4$,† and $NH_4Br.Br_2$.‡ No perhalides of the salts of the anilides have hitherto been described, but perhalides of other organic halides have frequently been observed, of which the following are examples: $C_6H_5N.NBr.Br_2$;§ $(C_9H_7N)_2HBr.Br_4$;‖ $C_6H_5(CH_3)_3NI.I_2$; $C_6H_5(CH_3)_3NI.I_4$; and $C_6H_5.C_2H_5(CH_3)_2NI.I_6$.¶

Method of Analysis. — In order to determine total bromine the weighed sample was treated with dilute ammonia, and in no case were the products analyzed which did not give the unaltered anilide with a correct melting-point. The solutions were then acidified with nitric acid, and the bromine determined by means of Volhard's** volumetric method. In another sample free bromine was determined by weighing the substance into a solution of potassium iodide and then titrating the liberated iodine with a tenth-normal sodium thiosulphate solution. From the difference the hydrobromic acid was calculated. Total iodine was also determined by Volhard's method, the free iodine having been converted into hydriodic

* Wells, Amer. Jour. Sci., xliii, 27.
† Wells and Wheeler, Ibid., xliv, 43.
‡ Roozeboom, Ber. d. chem. Ges., xiv, 2398.
§ Hantzsch, Ibid., xxviii, 2754.
‖ Grimaux, Bull. Soc. Chim. (Paris), xxxviii, 127.
¶ Geuther, Ann. Chem. (Liebig), ccxl, 66.
** Ann. Chem. (Liebig), cxc, 1.

acid by means of a solution of sodium arsenate in sodium bicarbonate. Free iodine was determined in a separate sample by means of the sodium thiosulphate solution, and the hydrogen iodide by difference.

Experiments with Metanitroacetanilide.

The 1 : 1 Hydrobromide, $C_6H_4.NO_2.NHCOCH_3.HBr$, was obtained as a colorless crystalline precipitate when hydrobromic acid gas was led into a chloroform solution of the anilide. It was dried on paper in the air.

	Found. I.	Found. II.	Calculated for $C_8H_8N_2O_3.HBr$.
HBr	30.5	30.8	30.9

The 2 : 1 Hydrobromide, $(C_6H_4.NO_2.NHCOCH_3)_2.HBr$.—This and the preceding salt were described in the preliminary paper.* It seems to be formed when the 1 : 1 salt is treated with glacial acetic acid, since perhalides of this salt were invariably obtained when bromine was added to the 1 : 1 salt in the presence of glacial acetic acid.

The Trihalide $(C_6H_4.NO_2.NHCOCH_3)_2.HBr.Br_2$. —2.5 g. of the 1 : 1 hydrobromide were covered with 25 g. of glacial acetic acid (containing some hydrobromic acid) and 3 g. of bromine added. On warming gently, filtering and cooling, beautiful light orange-colored flattened prisms separated. These were washed with chloroform and dried by pressing on filter-paper.

	Found.	Calculated for $C_{16}H_{16}N_4O_6.HBr.Br_2$.
Br (total) . . .	39.2	39.9
Br (free) . . .	26.2	26.6
HBr	13.1	13.4

The Pentahalide, $(C_6H_5.NO_2.NHCOCH_3)_2.HBr.Br_4$, was prepared by suspending the 1 : 1 hydrobromic acid salt in chloroform and adding bromine in the proportion of 1 molecule of the salt to about 12 atoms of bromine. Solution was effected by warming and adding small quantities of glacial

* Loc. cit.

acetic acid. On filtering and cooling, deep orange-colored prisms separated (analysis I). This compound was also obtained when 3.5 g. of the 1 : 1 salt were mixed with 11 g. of bromine in 13.8 g. of glacial acetic acid containing a little hydrobromic acid gas (analysis II).

The crystals that separated from the solution were washed with chloroform containing a little bromine. The material for analysis was dried on paper as rapidly as possible.

	Found. I.	Found. II.	Calculated for $C_{16}H_{16}N_4O_6.HBr.Br_4$.
Br (total)	52.7	51.2	52.5
Br (free)	42.6	40.4	42.0
HBr	10.2	10.8	10.6

The Heptahalide, $(C_6H_4.NO_2.NHCOCH_3)_2.HBr.Br_6$, was obtained by suspending 3.5 g. of the 1 : 1 hydrobromic acid salt in 7.8 g. of cold glacial acetic acid (containing hydrobromic acid); to this 58.8 g. of bromine were then added and the whole warmed to a blood heat. On cooling to $-10°$ long brick-red needles separated. These were washed free from glacial acetic acid by means of bromine which had been cooled to $-10°$. The material was drained on the pump, then on a porous plate, and finally pressed on paper (analysis I). A portion was exposed somewhat longer than I to the air (analysis II).

	Found. I.	Found. II.	Calculated for $C_{16}H_{16}N_4O_6.HBr.Br_6$.
Br (total)	61.0	61.3	60.8
Br (free)	53.5	53.0	52.1
HBr	7.5	8.4	8.8

Experiments with Parabromacetanilide.

The 2 : 1 Hydrobromide, $(C_6H_4Br.NHCOCH_3)_2.HBr$. — This and not the 1 : 1 salt was obtained when a chloroform solution of the anilide was treated with hydrobromic acid gas. It consisted of colorless needles.

	Found. I.	Found. II.	Calculated for $C_{16}H_{16}N_2O_2Br_2.HBr$.
HBr	15.4	15.9	15.9

The Trihalide, $(C_6H_4.Br.NHCOCH_3)_2.HBr.Br_2$, was obtained by adding ligroïn to a solution of the above hydrobromic acid salt in a mixture of ethyl acetate, chloroform, and bromine. The precipitate thus produced was crystallized from chloroform containing some glacial acetic acid. Beautiful, flattened, light-orange colored prisms separated.

	Found.	Calculated for $C_{16}H_{16}N_2O_2Br_2.HBr.Br_2$.
Br (total) . . .	35.8	35.9
Br (free) . . .	24.9	23.9
HBr	10.9	12.1

The Pentahalide, $(C_6H_4.BrNHCOCH_3)_2.HBr.Br_4$, was obtained by suspending the salt in chloroform, adding a large excess of bromine, and then warming with the addition of small quantities of glacial acetic acid until the whole dissolved. On cooling, small flattened crystals separated. These had a deep orange color.

	Found. I.	Found. II.	Calculated for $C_{16}H_{16}N_2O_2Br_2.HBr.Br_4$.
Br (total)	46.2	47.5	48.2
Br (free)	36.3	36.3	38.6
HBr	9.8	11.3	9.7

Experiments with Acetanilide.

The 2 : 1 Hydroiodide, $(C_6H_5.NHCOCH_3)_2.HI$, separated from a solution of acetanilide in ethyl acetate in the form of shining colorless scales, when hydrogen iodide was led into the solution.

	Found.	Calculated for $C_{16}H_{18}N_2O_2.HI$.
HI	32.2	32.1

The Trihalide, $(C_6H_5.NHCOCH_3)_2.HI.I_2$. — A solution of 4.1 g. of the above salt, with 2.6 g. iodine in 15 g. of glacial acetic acid deposited ruby-red crystals. These were analyzed with the following result:

	Found.	Calculated for $C_{16}H_{18}N_2O_2.HI.I_2$.
I (total) . . .	58.0	58.4
I (free) . . .	39.0	38.9
HI	19.1	19.6

The Pentahalide, $(C_6H_5.NHCOCH_3)_2.HI.I_4$, was obtained from a glacial acetic-acid solution of the constituents. It forms glistening prisms of a deep reddish-brown color with the lustre of iodine. They transmit a deep red-brown light.

	Found.	Calculated for $C_{16}H_{18}N_2O_2.HI.I_4$.
I (total) . . .	70.1	70.0
I (free) . . .	57.4	56.0
HI	12.8	14.1

THE ACTION OF ACID CHLORIDES ON THE SILVER SALTS OF THE ANILIDES.*

By H. L. WHEELER and B. B. BOLTWOOD.

In this paper we shall describe the action of benzoyl chloride on silver formanilide, on silver 2-4 dichlorformanilide, and on silver formorthotoluide. We shall show that these reactions resulted in the formation of diacid anilides and a diacid toluide, and that these diacid derivatives have the structure represented by the general formula

$$R{-}N{<}^{CHO}_{COC_6H_5}.$$

Some experiments on the action of chlorcarbonic ethylester on the silver salts of formanilide and formorthotoluide are also given.

If the reactions with benzoyl chloride are viewed as direct double decompositions, the following general equation will represent the formation of the diacid anilides, provided the silver salts have the metal joined to nitrogen:

$$R{-}N{<}^{CHO}_{\boxed{Ag + Cl}\,COC_6H_5} = R{-}N{<}^{CHO}_{COC_6H_5} + AgCl.$$

This view seems to be confirmed by the action of alkali or acids on the diacid anilides and toluide. This action consists in the removal of the formyl group, leaving the benzoyl radical attached to the $R{-}N{<}^{H}$ group, and shows that the structure of the diacid anilides is best represented by the formula used above. It may be represented by the following equation:

$$R{-}N{<}^{\boxed{CHO + HO}\,H}_{COC_6H_5} = R{-}N{<}^{H}_{COC_6H_5} + HOCHO.$$

* Amer. Chem. Jour., xviii, No. 5, May, 1896.

On the other hand, if the diacid anilides were oxygen derivatives, and if they had the structure

$$R—N{=}C{<}^{H}_{O.COC_6H_5},$$

corresponding to the pseudoform of the anilide, it would be difficult to see how the formyl group could be removed, leaving the benzoyl radical attached to the group $R—N{<}^{H}$, as shown above.

From the above considerations, we are led to believe that the diacid anilides are nitrogen derivatives. It follows, then, that the silver salts of the anilides behave with benzoyl chloride as if they had the structure $R—N{<}^{CHO}_{Ag}$, that is, as if the silver was joined to nitrogen. This behavior is remarkable, since the results obtained by the study of the action of alkyl halides on these salts are in direct opposition to this view. The work of Comstock,* with Kleeberg,† Wheeler ‡ and Clapp § has shown that these salts give imidoethers with alkyl halides. It was therefore concluded that the silver in these compounds is joined to oxygen, their structure being represented by the formula $R—N{=}C{<}^{H}_{OAg}$, and the general reaction represented as a direct double decomposition, as follows:

$$R—N{=}C{<}^{H}_{O}\boxed{Ag + I}CH_3 = RN{=}C{<}^{H}_{OCH_3} + AgI.$$

It is not our intention to discuss in this article the probable structure of the silver salts, but to call attention to the fact that these salts react as if they were derivatives of both the normal and pseudoform of the anilide. In other words, if we consider the double decomposition or substitution theory alone, these salts behave as if they had two structures. Questions of this nature, of so-called tautomeric reactions, have re-

* Ber. d. chem. Ges., xxiii, 2274.
† Amer. Chem. Jour., xii, 493.
‡ Ibid., xiii, 514.
§ Ibid., xiii, 525.

ceived considerable attention from Nef* and his co-workers in recent years. Nef has plainly shown, in his series of elaborate researches on tautomerism, that reactions of this nature involve not alone a double decomposition or substitution, but also an intermediate addition. We refer especially to his last article on this subject,† and also to his work published in 1892, where he refers to the different behavior of the sodium and silver salts of the anilides with alkyl halides, and decides that it is very improbable that these salts differ in their constitution, and that, in one case, an addition must take place.‡

It is now evident that although in the action of alkyl halides or of acid chlorides on the silver salts, a double decomposition may take place, such cannot be the case in both. Evidently in one case, and possibly in both, an intermediate addition is involved. The experimental evidence thus far obtained indicates that in the reactions described in this paper the acid chloride first forms an addition-product with the silver salt. This addition-product then separates silver chloride with the formation of the diacid anilide. That a silver salt can add hydrogen chloride and hydrogen sulphide without immediate separation of silver chloride or sulphide has been shown in the beautiful work of Nef on silver fulminate.§ The addition of benzoyl chloride to the silver salts of the anilides seems to be another example of this peculiar union.

If this is indeed the case, it does not necessarily favor the assumption that the silver salts of the anilides are derivatives of the pseudoform of the anilide, nor that addition takes place as follows:

$$\mathrm{HC}\begin{array}{l}{/\!\!/}\mathrm{N{-}R}\\ \diagdown\mathrm{OAg}\end{array} + \mathrm{ClCOC_6H_5} = \begin{array}{l}\mathrm{C_6H_5CO{-}N{-}R}\\ \qquad\quad\diagup\\ \qquad\mathrm{HC{-}Cl}\\ \qquad\quad\diagdown\\ \qquad\qquad\mathrm{OAg}\end{array}$$

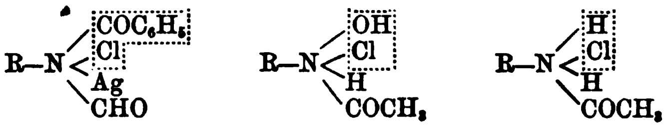
* Amer. Chem. Jour., xi, 1; xii, 379; xiii, 422. J. prakt. Chem. [2], xlii, 161. Ann. Chem. (Liebig), cclxvi, 52; Ibid., cclxx, 267; Ibid., cclxxvi, 200; Ibid., cclxxvii, 59 and 162; Ibid., cclxxx, 263 and 291.

† Ann. Chem. (Liebig), cclxxxvii, 269.

‡ Proc. Amer. Acad., May, 1892, 102; and Ann. Chem. (Liebig), cclxx, 298.

§ Ann. Chem. (Liebig), cclxxx, 313.

For it is to be noticed that the addition of acid chloride to a silver salt of an anilide might well take place to the nitrogen entirely, the resulting product then being analogous to the hypochlorous acid addition first noticed by Witt,* and also to the salts of the anilides with the halogen acids.† The compounds being pentavalent nitrogen derivatives as follows:‡



That the structure of the silver salts of the anilides cannot be decided by their final reaction-products is shown by the above considerations, and it is again shown in the work that we have done so far with chlorcarbonic ethyl ester and silver formanilide. We shall show in the latter part of this paper that these substances gave both the oxygen derivative, phenylformimidoethyl ether or ethylisoformanilide, and the nitrogen compound formylphenylurethane from which we isolated phenylurethane. The action with silver formorthotoluide appears to be similar.

Work on the action of acid chlorides on other salts of the anilides is now in progress in this laboratory, and it is also intended to continue the present work on the silver salts, this having been interrupted by the departure of one of us from this laboratory.

Experimental Part.

Formylbenzanilide, $C_6H_5N<{CHO \atop COC_6H_5}$. — When dry silver formanilide § is suspended in a small amount of benzene

* Ber. d. chem. Ges., viii, 1226.

† Knorr, Ann. Chem. (Liebig), ccxlv, 375; Wheeler and Walden, Amer. Chem. Jour. xviii, 87.

‡ Pictet explains the formation of benzanilide from benzoyl chloride and form- or acetanilide, etc., by means of a similar addition of the acid chloride to the anilide. Ber. d. chem. Ges., xxiii, 3011.

§ This was prepared according to the directions of Comstock and Kleeberg, loc. cit.

and one molecular proportion of benzoyl chloride is added, the first evidence of a reaction begins with a slight warming. On stirring, the mass thickens until it becomes almost semi-solid, it then becomes more fluid and the odor of benzoyl chloride disappears. The action can be hastened by warming. On filtering and concentrating the benzene solution, silver chloride frequently separates, although the extract filters at first perfectly clear. The residue consists of an oil which on standing solidifies. When this mass is crystallized from alcohol, more silver chloride separates along with beautiful colorless needles of the diacid anilide. It sometimes takes several crystallizations from alcohol to free these crystals completely from silver. Attempts were made to isolate this supposed addition product which apparently is formed here, and which would explain the persistency with which silver chloride contaminates the product, but the reaction took place too rapidly to permit of the isolation of an addition-product suitable for analysis, even at the melting-point of benzene. The yield of formylbenzanilide is practically quantitative. Analysis of the diacid anilide dried over calcium chloride gave:

	Found.	Calculated for $C_{14}H_{11}NO_2$.
C	74.33	74.67
H	4.92	4.88
N	6.46	6.14

Formylbenzanilide is readily soluble in benzene and chloroform, less so in ether and alcohol, and difficultly in water. It melts at 112°. When it is treated with sodium hydroxide, the formyl group is removed and benzanilide melting at 162° is obtained. A mixture of benzanilide and formylbenzanilide can readily be distinguished when crystallized from alcohol. The former separates at first in needles, the latter forms a supersaturated solution, and on shaking deposits plates.

2–4 Dichlorformanilide, $C_6H_3Cl_2NH.CHO$. — This was prepared from acetanilide by chlorinating according to the method of Beilstein and Kurbatow.* From the pure dichloracetani-

* Ann. Chem. (Liebig), cxcvi, 215.

lide thus obtained the acetyl group was replaced by the formyl in the usual manner. 2–4 dichlorformanilide crystallizes from alcohol in colorless needles, which melt at 153°.

	Found.	Calculated for $C_7H_5NOCl_2$.
C	44.15	44.22
H	2.71	2.63

Silver 2–4 Dichlorformanilide, $C_6H_3Cl_2NAgCHO$, was obtained from the sodium salt in the same manner as silver formanilide. It separates as a white amorphous bulky precipitate, and as regards the action of light, it is the most stable silver salt of the anilides that we are familiar with. It was washed with water and dried over sulphuric acid.

	Found.	Calculated for $C_6H_3Cl_2NAgCHO$.
Ag	36.48	36.36

2–4 Dichlorformylbenzanilide, $C_6H_3Cl_2N<^{CHO}_{COC_6H_5}$.—To prepare this, the above silver salt was mixed with benzoyl chloride in proportion to their molecular weights, the operation being carried out as before in dry benzene. When the benzene solution was filtered and evaporated, an oil remained. This was taken up in 95 per cent alcohol. This left a residue apparently of silver chloride. On letting the alcoholic solution stand, more silver chloride separated; then the diacid anilide, first as an oil, and finally in bunches of colorless acicular prisms. These, on crystallizing from alcohol, melted at 77°. Analysis gave:

	Found.	Calculated for $C_{14}H_9Cl_2NO_2$.
C	57.09	57.14
H	3.17	3.06
N	4.83	4.76

2–4 Dichlorformylbenzanilide is readily soluble in benzene and in hot alcohol, but difficultly soluble in water.

2–4 Dichlorbenzanilide, $C_6H_3Cl_2N<^{H}_{COC_6H_5}$. — This was formed when 2–4 dichlorformylbenzanilide was boiled with

dilute hydrochloric acid, the resulting product was crystallized from strong alcohol. It melted sharply at 117°. Analysis gave:

	Found.	Calculated for $C_{13}H_9NOCl_2$.
N	5.11	5.26

2–4 Dichlorbenzanilide is only sparingly soluble in hot water, difficultly in cold alcohol, readily in hot, and easily in ether.

Formylbenzorthotoluide, $C_6H_4CH_3N<^{CHO}_{COC_6H_5}$. — The preparation of this from silver formorthotoluide and benzoyl chloride was precisely the same as we have described in the two preceding cases. The product showed the same tendency to retain silver. It was obtained from the benzene solution as an oil. This was dissolved in alcohol and the solution allowed to stand, when beautiful, thick, apparently rectangular plates, diagonally striated, separated. These on crystallizing from alcohol melted at 92°. Analysis gave:

	Found.	Calculated for $C_{15}H_{13}NO_2$.
C	75.12	75.31
H	5.64	5.43
N	5.87	5.85

Formylbenzorthotoluide is readily soluble in benzene and in warm alcohol, but difficultly soluble in water. Some of the analyzed material was treated with dilute sodium hydroxide, and the product then crystallized from dilute alcohol, when benzorthotoluide was obtained in colorless needles melting at 142°.

A comparison of the melting-points of the diacid derivatives, described in this paper, with those of the mono-acid anilides and toluides shows no strict regularity, except that the melting-points of the di-derivatives are lower than those of the benzoyl compounds. This will be seen from the following list:

	M. P.		M. P.
Formanilide	46°	Formorthotoluide . .	62°
Formylbenzanilide . .	112°	Formylbenzorthotoluide	92°
Benzanilide	163°	Benzorthotoluide . . .	142°

	M. P.
2–4 Dichlorformanilide . . .	153°
2–4 Dichlorformylbenzanilide .	77°
2–4 Dichlorbenzanilide . . .	117°

Action of Chlorcarbonic Ethylester on Silver Formanilide and on Silver Formtoluide.

Silver formanilide and chlorcarbonic ester were mixed in benzene solution in molecular proportions; the reaction took place rapidly and carbonic acid gas was given off. To complete the reaction, the whole was warmed on the water-bath. On filtering from silver chloride and evaporating the benzene solution, an oil was obtained; this was distilled at a pressure of 18 mm., when a small amount of phenylformimidoethyl ester or ethylisoformanilide * was obtained, which boiled at about 106° under these conditions. This substance was identified by its action with aniline, and also on standing alone exposed to the air. In both cases diphenylformamidine was obtained, melting at 136°. For comparison this imido-ether was made from the silver salt of formanilide with ethyl iodide. This product was found to be identical with that obtained from the chlorcarbonic ester reaction.

Phenyl 2–4 Dichlorphenylformamidine, $HC\langle{}^{/\!/ NC_6H_5}_{\backslash NHC_6H_3Cl_2}$.— This was formed when the above imido-ether was mixed with 2–4 dichloraniline. It crystallizes from benzene in bunches of minute colorless plates, which melt at 159°.

	Found.	Calculated for $C_{13}H_{10}N_2Cl_2$.
N	10.59	10.57

The residue left after the distillation of the imido-ether was treated with dilute hydrochloric acid and alkali, and then

* Described by Comstock and Clapp, loc. cit.

crystallized from ligroïn. This gave phenylurethane, melting at 52°. On extracting the silver chloride residue with water, diphenylformamidine hydrochloride was obtained.

In another experiment 30 g. of silver salt were taken, and an excess of chlorcarbonic ester was unintentionally used. In this experiment we succeeded in isolating phenylurethane in addition to the imido-ether and the amidine. The approximate quantities of these substances formed were as follows: 0.9 g. of diphenylformamidine hydrochloride, 5.0 g. of imido-ether, and 14 g. of oil, which we did not succeed in purifying. A small quantity of isonitril was formed, probably in the distillation. The oil evidently consisted of the expected formylphenylurethane, since, on warming with dilute sodium hydroxide and then crystallizing the product from ligroïn, phenylurethane was obtained, melting at 52°. The latter was positively identified by analysis:

	Found.	Calculated for $C_9H_{11}NO_2$.
C	65.60	65.45
H	6.74	6.66

Experiments with the silver salt of formorthotoluide and chlorcarbonic ethyl ester, conducted in the same manner as the preceding, gave orthotolylformimidoethyl ester, *s*-ditolyl urea, and a residue, presumably formyltolyl urethane, but we did not succeed in purifying this for analysis.

Orthotolylformimidoethyl Ester, $C_6H_4CH_3N{=}C{<}^{H}_{OC_2H_5}$.— This is an aromatic oil boiling at 101° at 12 mm. pressure. Analysis gave:

	Found.	Calculated for $C_{10}H_{13}NO$.
C	73.19	73.62
H	7.94	7.91

From the high-boiling fractions of the imido-ether a crystalline colorless substance separated. This was washed with ligroïn and analyzed.

	Found.	Calculated for $C_{15}H_{16}N_2O$.
C	74.44	74.37
H	7.11	7.43
N	11.06	11.57

Its melting-point, 256°, and the above analysis show that this substance was *s*-orthoditolyl urea.

I.—ON SOME MERCURY SALTS OF THE ANILIDES.*

By H. L. WHEELER and B. W. McFARLAND.

NUMEROUS investigators have had occasion to work with the sodium and silver salts of the anilides, and have used these compounds in syntheses, while little attention has been given to the mercury salts. Mercury acetanilide first prepared by Oppenheim and Pfaff † seems to be the sole representative of the mercury salts of the anilides that has been prepared. This compound has recently been examined by Piccinini, ‡ and he concludes that it is a mercurammonium derivative, since the mercury can be removed from it at ordinary temperature by means of sodium thiosulphate, potassium iodide, or ammonium bromide, thus differing from Pesci's § paramercurioacetanilide, which is not effected by these reagents.

The experiments of Piccinini, however, do not decide whether mercury acetanilide has the structure

$$
\begin{array}{lll}
\begin{array}{l}
\qquad COCH_3 \\
\quad / \\
C_6H_5N \\
\qquad >Hg \\
C_6H_5N \\
\quad \backslash \\
\qquad COCH_3
\end{array}
& \quad \text{or} \quad &
\begin{array}{l}
C_6H_5N{=}C.CH_3 \\
\qquad\quad \backslash \\
\qquad\quad O \\
\qquad\quad\ >Hg \\
\qquad\quad O \\
\qquad\quad / \\
C_6H_5N{=}C.CH_3
\end{array}
\end{array}
$$

The former structure corresponds to that generally accepted for the sodium salts of the anilides, the latter to that of the silver salts.

We are now prepared to show that formanilide and paraformtoluide give mercury salts, and that these salts—as well as mercury acetanilide—react with benzoyl chloride as if they had the metal joined to nitrogen. We have also found that

* Amer. Chem. Jour., xviii, No. 7, July, 1896.

† Ber. d. chem. Ges., vii, 624. ‡ Ibid., xxviii, R. 113. § Ibid., R. 112.

the action of bromine and iodine on mercury formanilide is similar to that of benzoyl chloride.

In the course of the above-mentioned reaction such mercuric halogen compounds as the following are directly obtained:

$$C_6H_5N<^{CHO}_{HgCl}, \qquad C_6H_5N<^{CHO}_{HgBr}, \qquad C_6H_5N<^{CHO}_{HgI}.$$

The reactions may be represented by the following equation in which hal represents halogen and X either C_6H_5CO—, Br, or I.

$$\begin{array}{l} \boxed{C_6H_5N<^{CHO}_{Hg} + \text{hal}}\,X = C_6H_5N<^{CHO}_{Hg\ \text{hal}} + C_6H_5N<^{X}_{CHO} \\ C_6H_5N\diagdown_{CHO} \end{array}$$

These halogen mercuric compounds represent a part of the mercuric salt united to halogen. They are undoubtedly nitrogen derivatives, being analogous to the well-known ammonia compound $H_2N-HgCl$, the so-called white precipitate, and to the aniline salts, $C_6H_5N<^{H}_{HgCl(Br)\ (or\ I)}$, $C_6H_5N<^{H}_{HgOCOCH_3}$, etc., described by Pesci.*

It is also to be noticed that in the above-mentioned reactions of the mercury salts, besides the halogen mercury compounds, nitrogen-substituted anilides are also formed. For example: Benzoyl chloride and mercury formanilide give formylbenzanilide, $C_6H_5N<^{CHO}_{COC_6H_5}$, in addition to chlormercury formanilide, $C_6H_5N<^{HgCl}_{CHO}$; and the diacid anilide when treated with alkali or dilute acid is decomposed into benzanilide,

$$C_6H_5N<^{H}_{COC_6H_5},$$

and formic acid. The diacid anilide, therefore, has both acid groups attached to nitrogen, since such a decomposition could only result from a nitrogen derivative, *i. e.*, $C_6H_5N<^{CHO}_{COC_6H_5}$. On the other hand, if the diacid anilide were an oxygen

* Gazz. chim., xxii [1], 378.

derivative, *i. e.*, $C_6H_5N{=}C{<}{}^{H}_{O.COC_6H_5}$, it is evident that the formyl group could not be removed without also removing the benzoyl radical, and we should get aniline, formic and benzoic acids instead of benzanilide. The decomposition of the diacid anilide, therefore, is to be represented as follows:

$$C_6H_5N\begin{matrix}\diagup \boxed{CHO + HO}H \\ \diagdown COC_6H_5\end{matrix} = C_6H_5N{<}{}^{H}_{COC_6H_5} + HOCHO$$

The above facts show that the mercury salts of the anilides have the mercury undoubtedly united to nitrogen, for were it joined to oxygen, it would be impossible to explain the formation of the halogen mercury compounds and the diacid anilides by the usual theory, in tautomeric reactions, of addition and separation, since in this case an assumption of an elaborate rearrangement would also be necessary.

The mercury salts are therefore to be represented by the following structure:

$$\begin{matrix} C_6H_5N\begin{matrix}\diagup CHO \\ \diagdown \end{matrix} \\ \qquad Hg \\ C_6H_5N\begin{matrix}\diagup \\ \diagdown CHO\end{matrix} \end{matrix} \quad \text{and not} \quad \begin{matrix} C_6H_5N{=}C\begin{matrix}\diagup H \\ \diagdown O\end{matrix} \\ \qquad\qquad Hg \\ C_6H_5N{=}C\begin{matrix}\diagup O \\ \diagdown H\end{matrix} \end{matrix}$$

Experimental Part.

Mercury Formanilide, *$(C_6H_5NCHO)_2Hg$*, is most conveniently prepared by dissolving formanilide and mercuric bromide in alcohol, then adding the calculated quantity of sodium ethylate, and diluting with water. The resulting precipitate (analysis I) can be crystallized from water (analysis II). It then separates in colorless needles which melt at about 194°. Mercury formanilide can also be obtained by use of mercuric nitrate and sodium ethylate, or by boiling an alcoholic solution of formanilide with mercuric oxide (analysis III) or mercurous oxide (analysis IV). It also results when sodium formanilide is boiled with mercurous nitrate.

	Found. I.	II.	III.	IV.	Calculated for $C_{14}H_{12}N_2O_2Hg$.
Hg . . .	45.0	45.2	46.1	45.4	45.4
N.	...	6.2	...	...	6.3

Chlormercury Formanilide, $C_6H_5N<{CHO \atop HgCl}$. — When mercury formanilide is suspended in benzene, and 1 molecule of benzoyl chloride is added, the reaction takes place, slowly in the cold, rapidly when warmed. On filtering and washing the residue with benzene, pure chlormercury formanilide remains (analysis I). This compound is also obtained when equal molecules of formanilide, mercuric chloride, and sodium ethylate are mixed in alcoholic solutions (analysis II). It crystallizes from water in shining colorless plates melting at 191° (analysis III).

	Found. I.	II.	III.	Calculated for $C_7H_6NOHgCl$.
Hg	...	56.4	56.5	56.3
Cl	9.6	9.9	...	9.9

Formylbenzanilide, $C_6H_5N<{CHO \atop COC_6H_5}$. —On concentrating the above-mentioned benzene solution, this diacid anilide is obtained in colorless, brittle prisms, which on recrystallizing from benzene melt at 112°. It crystallizes from water in needles, and when recrystallized from this solvent or from alcohol the melting-point does not change. Analysis gave:

	Found.	Calculated for $C_{14}H_{11}NO_2$.
C	75.27	74.67
H	4.93	4.88
N	6.10	6.22

When formylbenzanilide is treated with acids or alkalies, the formyl group is removed and benzanilide is formed. This was identified by its melting-point and general properties. It is to be noticed that this diacid anilide from mercury formanilide is identical in all its properties with formyl benzanilide obtained from silver formanilide and benzoyl chloride.*

* Amer. Jour. Chem., xviii, 381.

Brommercury Formanilide, $C_6H_5N<\begin{smallmatrix}CHO\\HgBr\end{smallmatrix}$, was obtained when mercury formanilide was suspended in carbon disulphide and 1 molecular proportion of bromine added. During this operation the whole was cooled with ice.

The residue was washed with carbon disulphide until colorless, dried in the air, and then analyzed (analysis I). Another portion was crystallized from dilute alcohol, from which it separated in bunches of radiating, yellow-white plates. The trace of color and the analysis indicate that in this operation a slight decomposition had taken place (analysis II).

	Found. I.	Found. II.	Calculated for $C_7H_6NOHgBr$.
Hg	. . .	50.2	50.0
Br	19.9	19.4	20.0

The above-mentioned carbon disulphide solution was evaporated over sulphuric acid by means of a pump. This left a brown or black mass. The color was not removed from the solution in carbon disulphide or ether by boiling with animal charcoal. Attempts to isolate the unstable formylbromaminobenzene,* $C_6H_5N<\begin{smallmatrix}Br\\CHO\end{smallmatrix}$, were therefore abandoned. We then boiled the residue with water. This extracted a colorless substance containing bromine, crystallizing in needles from hot water and melting at 119°. It was, therefore, the expected parabromformanilide, resulting probably from the molecular rearrangement of formylbromaminobenzene.

Iodmercury Formanilide, $C_6H_5N<\begin{smallmatrix}CHO\\HgI\end{smallmatrix}$. — Molecular proportions of mercury formanilide and iodine were mixed in carbon disulphide, and the whole was allowed to stand for twenty-four hours. The residue which remained was filtered, washed with carbon disulphide, dried, and analyzed. It decomposed on boiling with water.

	Found.	Calculated for C_7H_6NOHgI.
I	28.5	28.4

* Slosson, Ber. d. chem. Ges., xxviii, 3268.

The carbon disulphide filtrate from iodmercury formanilide was evaporated to dryness at ordinary temperature. A black residue resulted as in the case of the bromine reaction. From this residue we succeeded in extracting a small amount of paraiodformanilide by boiling with water. On crystallizing from water it gave the correct melting-point, 108°.

In another experiment chloroform was used instead of carbon disulphide, and an excess of mercury formanilide was present. We succeeded in this experiment in showing the presence of a substance which easily liberated iodine, but which was not obtained in pure condition. This unstable compound was probably iodisoformanilide or formyliodaminobenzene which Comstock and Kleeberg * obtained from the silver salt of formanilide. On warming this with formic acid, then crystallizing from water as they describe, we obtained paraiodformanilide, crystallizing from water in colorless needles, and melting at 108°.

Mercury Formanilide Acetate, $C_6H_5N<\begin{matrix}CHO\\HgOCOCH_3\end{matrix}$. — When mercuric acetate is mixed with formanilide in alcoholic solution, acetic acid is liberated. On concentrating the solution bunches of colorless slender prisms of the above compound separate. Again, on dissolving dry mercuric acetate in a very strong alcoholic solution of formanilide and then warming, the whole suddenly solidifies. When this mass is crystallized from strong alcohol, the same colorless prisms result:

	Found.	Calculated for $C_9H_9NO_3Hg$.
Hg	53.1	52.8

Mercury Formparatoluide, $(CH_3C_6H_4NCHO)_2Hg$. — 10 g. of formparatoluide and 14 g. of mercuric bromide were dissolved in 40 c. c. of 95 per cent alcohol, then 1.7 g. of sodium also in 40 c. c. of alcohol were added. This, on shaking, gave a clear solution, to which an equal volume of water was added. The mercury salt then separated in a thick mass of crystals. These were washed with alcohol (analysis I). A portion

* Amer. Chem. Jour., xii, 493.

crystallized from water gave colorless needles (analysis II). Another specimen was prepared by using mercuric chloride instead of the bromide, and this was crystallized from 50 per cent alcohol and analyzed (analysis III).

	Found.			Calculated for $C_{16}H_{16}N.O_2Hg$.
	I.	II.	III.	
Hg . . .	43.48	43.25	43.00	42.73

Chlormercury Formparatoluide, $CH_3C_6H_4N<^{CHO}_{HgCl}$. — This was obtained as a residue when the above mercury salt, suspended in benzene, was treated with benzoyl chloride (analysis I). It crystallizes from water in colorless needles, and the analysis indicates that in this treatment a slight decomposition takes place (analysis II).

	Found.		Calculated for $C_8H_8NOHgCl$.
	I.	II.	
Hg	54.19	52.53	54.20

Formylbenzparatoluide, $CH_3C_6H_4N<^{CHO}_{COC_6H_5}$. — The benzene solution from chlormercury formparatoluide was evaporated, and the residue taken up in ether. This operation was repeated. The material was then crystallized from a mixture of ligroïn and ether, when colorless prisms were obtained melting at 101°.

	Found.	Calculated for $C_{15}H_{13}NO_2$.
N	5.36	5.85

On warming this product with dilute sodium hydroxide, the formyl group was removed and benzparatoluide was obtained.

Acetbenzanilide, $C_6H_5N<^{COCH_3}_{COC_6H_5}$. — The preparation of this compound was perfectly analogous to that of formylbenzanilide and formylbenzparatoluide. Mercury acetanilide, best prepared according to the directions of Piccinini,* and benzoyl chloride were mixed in molecular proportions in benzene. On filtering, evaporating the benzene solution, and crystalliz-

* Loc. cit.

ing the residue from dilute alcohol, an oil separated which changed to long needles, melting at 68°. When this material was crystallized three times from dilute alcohol, the melting-point remained constant.

	Found.	Calculated for $C_{15}H_{13}NO_2$.
N	5.81	5.85

On warming with dilute sodium hydroxide and then crystallizing from alcohol, pure benzanilide was obtained, melting from 162° to 163°. Here, also, as in the case of formylbenzanilide and formylbenzparatoluide, alkali removes the lower acid group.

Mercury Symmetrical Tribromacetanilide, $(C_6H_2Br_3NCOCH_3)_2Hg$.—This was prepared like mercury acetanilide, except that dilute alcoholic solutions were used. The precipitate, washed with water and then with alcohol, gave an analysis 22.4 per cent of mercury instead of 21.4 per cent. It crystallizes from 50 per cent alcohol in bunches of needles.

Mercury Formyl-a-naphthylamine, $(C_{10}H_7NCHO)_2Hg$.—This was prepared like mercury formparatoluide. It gave colorless needles, which were washed with water, and then with hot alcohol. A mercury determination gave 36.4 per cent mercury instead of 37.6 per cent.

It will be noticed that, as the solubility of the anilide in water or dilute alcohol decreases, pure mercury salts are to be obtained only with difficulty. For this reason acetparatoluide and benzanilide did not give mercury salts of even approximate purity by the above methods.

New Haven, May, 1896.

ON THE USE OF ANTIMONY TRICHLORIDE IN THE SYNTHESIS OF AROMATIC KETONES.*

By WILLIAM J. COMSTOCK.

Among the reagents which may be used in special cases instead of aluminium chloride in syntheses involving the separation of hydrochloric acid, there is no record, as far as I have found, of the use of antimony trichloride. Indeed the applicability of aluminium chloride is so general that one would hardly search deliberately for a condensing-agent to replace it, although its use does involve certain objectionable features on account of its extremely hygroscopic properties. It is certainly more agreeable to handle antimony trichloride, which has moreover comparative cheapness in its favor, as well as the advantage that in case it has absorbed moisture by long standing or exposure, the anhydrous chloride can be readily recovered. Should it be a question of working on a large scale where the expense is the important, perhaps the one essential, consideration, the use of antimony trichloride would undoubtedly be preferred, as it can be recovered from the product of the reaction by evaporation of the hydrochloric acid solution used to free the ketone from antimony, and subsequent distillation of the residue. I have found that a mixture of an acid chloride with an aromatic hydrocarbon and antimony trichloride, evolves hydrochloric acid when heated, and that for the synthesis of benzophenone and its homologues the method can be used with excellent results. The yields compare favorably with those obtained by Elbs,† who made a careful study of the Friedel and Crafts reaction for the synthesis of the same ketones. The reaction does not

* Amer. Chem. Jour., xviii, No. 7, July, 1896.

† J. prakt. Chem., xxxv, 465.

take place at ordinary temperature, and cannot be successfully applied with low-boiling chlorides, as, for instance, to the synthesis of acetophenone. It is not my intention to work through the list of ketones to whose synthesis the method might be applied; but I give experiments in three typical cases, leading to well-known compounds, to show the yields, advantageous proportions, etc. Without doubt the method can be used to condense any acid chloride having a moderately high boiling-point, with an aromatic hydrocarbon. For the preparation of ketones from the phenol ethers the method can be used, but its advantages are rather doubtful on account of the saponifying action of the antimony trichloride.

Gattermann, Ehrhardt, and Maisch * have made many ketone syntheses with the phenol ethers according to the method of Friedel and Crafts, but as the yields are not given, I have no means of comparing the two condensing-agents.

Hartmann and Gattermann † have shown that the phenol ethers are saponified by aluminium chloride, and state that this causes a loss in the preparation of the ketones. The saponifying action of antimony trichloride on the phenol ethers reduces the yield of ketone far below that found in the experiments with hydrocarbons given below, although the reaction takes place more readily. I have obtained about 40 per cent of the theoretical yield of pure *p*-methoxybenzophenone, and doubtless the yield could be improved by a careful study of the conditions. Indeed, by diluting with carbon bisulphide the amount of bye-products is reduced, but the time required is much longer. As to the use of antimony trichloride for the synthesis of compounds other than ketones, I have made no careful study, but will mention a few observations that seem of interest in this connection. It is not possible to prepare triphenylmethane from chloroform by this method; there is no evolution of hydrochloric acid when chloroform, benzene, and antimony trichloride are heated, even when large quantities of chloride are used. The reaction between benzal chloride and benzene seems to take place very readily, but the

* Ber. d. chem. Ges., xxiii, 1199.

† Ibid., xxv, 3531.

product contains a large amount of dark resinous matter, and so much that is not triphenylmethane that I have not studied the case further.

Syntheses with benzyl chloride in presence of antimony trichloride are not to be recommended. To be sure, diphenylmethane can be prepared with a yield of about 12 per cent, but the greater part of the benzyl chloride is converted into more complicated, high-boiling compounds, apparently the same anthracene derivatives that are formed when benzyl chloride is treated with aluminium chloride. In consideration of the possibility, though a remote one, of a direct synthesis of the ethereal salts from ethyl chlorcarbonate, I have made one experiment, with paraxylene. But the result showed that the reaction takes place in the same way as with aluminium chloride, *i. e.*, carbonic acid is given off together with the hydrochloric acid, and the product of the reaction is a mixture of unaltered paraxylene with higher-boiling hydrocarbons, but no ethereal salt.

Smith and Davis * have described addition-products of antimony trichloride with benzene and naphthalene, compounds having the composition of two molecules of hydrocarbon to three molecules of antimony trichloride, and it is worth mentioning that aluminium chloride and antimony trichloride are the two metallic chlorides with which "molecular" compounds of the aromatic hydrocarbons have been obtained. Whether this has any connection with the syntheses which can be carried out in presence of these chlorides is doubtful.

Experimental.

In conducting the operation, the mixture is heated in a flask with reflux-condenser, either by a direct flame, or better by means of a paraffin or other bath. The only precautions to be taken are to use substances free from water, to protect the mixture from the moisture of the air during the operation by means of a calcium-chloride tube, and to avoid raising the

* J. Chem. Soc., xli, 411.

temperature too rapidly during the early part of the operation. The evolution of hydrochloric acid is rapid at 140°. This is true in the cases given below, as well as in other cases where the reaction was tried as a test-tube experiment only, without working up the product. The temperature of the bath is gradually raised as high as 200°. When the evolution of gas stops, and the odor of the acid chloride has disappeared, the mixture is washed with strong hydrochloric acid in a separatory funnel until the antimony is entirely removed. The ketone is then taken up in ether, dried over potassium carbonate, and finally distilled. Should there be difficulty in getting the ketone to separate from the acid solution, it can be taken up in ether at once, but in this case it requires repeated shaking of the ethereal solution with hydrochloric acid to remove the antimony trichloride. In carrying out the reaction with small quantities it is, however, desirable to take up in ether at once. For removing the antimony trichloride from the ketones it is also possible to use a strong solution of potassium or calcium chloride, acidified with hydrochloric acid.

Benzophenone.

Benzoyl chloride reacts more slowly with benzene than it does with the higher hydrocarbons. It is impossible to carry out the reaction with a small proportion of antimony trichloride, as the temperature of the mixture cannot be raised sufficiently high. With 56 g. of benzoyl chloride, 32 g. of benzene, and 75 g. of the trichloride, the reaction required forty hours for its completion. The yield of pure benzophenone, boiling at 306–308°, was 51 g. or 70 per cent of the theoretical. The proportions given in the following experiment are to be recommended, as they enable one to carry out the reaction within reasonable time limits:

112 g. C_6H_5COCl
70 g. C_6H_6
300 g. $SbCl_3$

The reaction was completed in about twelve hours. The yield was 108 g. of benzophenone boiling at 306°–308°, *i. e.* 74 per cent of the theoretical.

The yield of crystallized, but not carefully rectified ketone is of course larger. Elbs gives the yield of "pure crystallized ketone," obtained by the Friedal and Crafts reaction, as 70 to 75 per cent of the theoretical.

Benzoyl Chloride and Toluene.

Experiment 1. — The mixture used was made up thus:

56 g. C_6H_5COCl
40 g. C_7H_8
15 g. $SbCl_3$

The time required to complete the reaction was forty-two hours. The yield of mixed ortho- and paratolylphenyl ketones, 56 g. or 72 per cent of the theoretical, boiling between 177° and 182°, at a pressure of 16 mm.

Experiment 2. — The mixture used in this case was:

56 g. C_6H_5COCl
40 g. C_7H_8
60 g. $SbCl_3$

The reaction was completed in five hours; yield of mixed ortho- and para-ketones, 62 g. or 80 per cent of the theoretical. According to Elbs, the yield of mixed ortho- and paraketones runs up as high as 95 per cent of the theoretical, when aluminium chloride is used. As to the proportion of ortho and para in the mixture, there is apparently a higher percentage of ortho-ketone formed when antimony trichloride is used. Elbs states that from his mixture of the two ketones he could obtain 80 to 95 per cent of pure paratolylphenyl ketone, and that the mixture "caked" at ordinary temperature. I obtained 64 per cent of pure paraketone from the mixture. The separation is of course incomplete, but the mixture of ketone, which I obtained, did not "cake" till it was cooled with ice.

Paraxylylphenylketone.

The following mixture was used:

28 g. C_6H_5COCl
22 g. paraxylene
20 g. $SbCl_3$

The reaction was completed in about six hours. The yield of pure ketone, boiling between 317°–319°, was 34 g., or 80 per cent of the theoretical.

In another experiment the same amounts of benzoyl chloride and paraxylene were used with 30 g. of the trichloride. The reaction was completed in 4½ hours; yield 31 g. or 74 per cent of the theoretical. Elbs obtained 60 to 70 per cent.

NEW HAVEN, May, 1896.

ON DIACID ANILIDES.*

BY H. L. WHEELER.

FOR convenience of reference, diacid anilides may be divided into two classes. The first class will consist of those which have identical acid groups, such as diacetanilide,

$$C_6H_5.N{<}{\genfrac{}{}{0pt}{}{COCH_3}{COCH_3}},$$

while the second class will contain those with unlike acid groups, and will be referred to as mixed diacid anilides, formylacetanilide, for example,

$$C_6H_5.N{<}{\genfrac{}{}{0pt}{}{CHO}{COCH_3}}.$$

Diacid anilides of the first class can be prepared by acting on the monoacid anilides with acid anhydrides † ‡ or acid chlorides. § They have also been obtained from the sodium salts of the anilides and acid anhydrides ‖ and from the mustard oils.¶

Diacid anilides of the second class have not been obtained by any of the above methods. They could not be prepared by acting on the monoacid anilides ** or their sodium salts †† with acid chlorides, while attempts to prepare them by acting on the anilides with acid anhydrides, formanilide, and acetic anhydride, for example, did not give pure products. However, the above method can be used with success in the preparation of what may be called semi-diacid anilides, since oxanilide and oxalparatoluide give monoacetyloxanilide and monoacetyloxalparatoluide, ‡‡ *i. e.*,

* Amer. Chem. Jour., xviii, No. 8, October, 1896.
† Bistrzycki and Ulffers, Ber. d. chem. Ges., xxvii, 91.
‡ Tassinari, Ibid., R, xxvii, 581.
§ Kay, Ibid., xxvi, 2853.
‖ Blacher, Ibid., xxviii, 2356.
¶ Kay, Ibid., xxvi, 2848.
** Pictet, Ibid., xxiii, 3014.
†† Paal and Otten, Ibid., xxiii, 2587.
‡‡ Tassinari, Loc. cit.

$$\begin{array}{l}CO.N<\begin{array}{l}COCH_3\\ C_6H_5\end{array}\\ |\\ CO.NHC_6H_5\end{array} \quad \text{and} \quad \begin{array}{l}CO.N<\begin{array}{l}COCH_3\\ C_6H_4CH_3\end{array}\\ |\\ CO.NHC_6H_4CH_3\end{array}$$

In two former papers* from this laboratory the action of benzoyl chloride on the silver and mercury salts of the anilides was described. It was then shown that these salts could be used for the synthesis of the hitherto inaccessible mixed diacid anilides, and that both silver and mercury formanilide gave the same compound, *i. e.*, formylbenzanilide $C_6H_5N<\begin{array}{l}CHO\\ COC_6H_5\end{array}$, etc.

In the present paper it will be shown that the action of aliphatic acid chlorides on silver formanilide and mercury acetanilide is perfectly analogous to that of benzoyl chloride; that the formation of mixed diacid anilides is general; and that these diacid anilides react with alkali invariably with the separation of the lower acid radical and formation of the anilide of the higher acid, as follows:

$$C_6H_5N<\begin{array}{l}CHO\\ COCH_3\end{array} + NaOH = C_6H_5N<\begin{array}{l}H\\ COCH_3\end{array} + NaOCHO$$

By this reaction the mixed diacid anilides are shown to be nitrogen derivatives, and, since diacetanilide is formed from the mercury salt of acetanilide in precisely the same manner as the mixed diacid anilides, it is probable that the anilides of both classes have an analogous structure.

In the latter part of this paper a notice is given of the action of acetyl and benzoyl chlorides on silver and mercury benzamide, and it is the intention of the author to extend the work to salts of other amides and imides.

From silver formanilide and mercury acetanilide the following series of diacid anilides have now been prepared in this laboratory:

* Wheeler and Boltwood, Amer. Chem. Jour., xviii, 381; Wheeler and McFarland, Ibid., xviii, 540.

Acetylacetanilide or Diacetanilide,

Formylacetanilide,	Acetylpropionanilide,
Formylpropionanilide,	Acetyl-*n*-butyranilide,
Formyl-*n*-butyranilide,	Acetylisovaleranilide,
Formylstearanilide,	Acetylpalmitanilide,
Formylbenzanilide,	Acetylbenzanilide.

Method of Preparation.

Silver formanilide or mercury acetanilide was suspended in dry ether or benzene and 1 molecular proportion of acid chloride was added. In the case of the mercury salts it was found convenient to use only 1 molecular proportion of acid chloride, since, by this means, the presence of mercuric chloride in the extract was largely avoided. The action then takes place chiefly as follows:

$$\boxed{C_6H_5N\genfrac{}{}{0pt}{}{\diagup COCH_3}{\diagdown Hg \qquad Cl}}\,COR = C_6H_5N\genfrac{}{}{0pt}{}{\diagup COCH_3}{\diagdown COR} + C_6H_5N\genfrac{}{}{0pt}{}{\diagup COCH_3}{\diagdown HgCl}$$
$$C_6H_5N\diagdown COCH_3$$

The action begins immediately with evolution of heat, and is complete in the case of the lower acid chlorides in a few minutes. After filtering from the silver chloride or the halogen mercuric compound, the filtrates in the case of the lower acid derivatives were shaken with water, and on evaporating the solvent the diacid anilides were obtained as oils. The purification and properties of these products are described below.

Acetylacetanilide or Diacetanilide, $C_6H_5N<^{COCH_3}_{COCH_3}$.—The preparation of this compound has received considerable attention. Bistrzycki and Ulffers * have carefully investigated the formation from acetanilide and acetic anhydride, and conclude that it is not to be obtained in a pure condition by the method of Reverdin and de la Harpe.† They have shown that it cannot be obtained from aniline and acetic acid as stated by

* Loc. cit.

† Ber. d. chem. Ges., xxii, 1006.

Gumpert,* and they also call attention to the fact that Krafft and Karsten † have shown that Hofmann ‡ did not obtain this compound from phenyl mustard oil and acetic acid. They state that they obtained diacetanilide first in April, 1893. They were anticipated, however, by Kay, § who prepared this compound from phenyl mustard oil and acetic anhydride, as well as from acetanilide and acetyl chloride. Its preparation, according to the method of Bistrzycki and Ulffers has been confirmed by Tassinari, ‖ while Blacher ¶ obtained it from sodium acetanilide and acetic anhydride. The work of the later investigators confirms that of Kay, and they refer to him for the properties of this compound. He obtained this diacid anilide as a clear colorless oil, boiling at 150° at 16 mm. pressure and solidifying to a mass of crystals, which on crystallizing from ligroïn melted at 37°.

The same compound results by acting on mercury acetanilide with acetyl chloride. The product obtained from the benzene solution, in this case, was an oil which boiled at 150° at 17 mm. pressure, and the distillate soon solidified to a colorless mass of crystals, which on crystallizing from ligroïn separated in eight-sided plates, melting at 37°. On warming with a dilute alcoholic solution of sodium hydroxide, acetanilide was formed.

Formylacetanilide, $C_6H_5N<\begin{matrix}CHO\\COCH_3\end{matrix}$. — This was obtained as an oil which soon solidified. It was crystallized from a mixture of ether and ligroïn, by evaporation under diminished pressure, when beautiful, colorless, prismatic crystals were obtained, melting at 56°.

	Found.	Calculated for $C_9H_9NO_2$.
N	8.59	8.58

Formylacetanilide is readily soluble in alcohol, ether, and benzene, but difficultly in ligroïn. On boiling with dilute

* J. prakt. Chem. [2], xxxii, 294.

† Ber. d. chem. Ges., xxv, 460.

‡ Ibid., iii, 770.

§ Loc. cit.

‖ Loc. cit.

¶ Loc. cit.

sodium hydroxide it dissolves, and, on cooling, acetanilide separates in plates melting at 114°.

Formylpropionanilide, $C_6H_5N<{CHO \atop COCH_2CH_3}$. — The product of the action of propionyl chloride on both silver and mercury formanilides, in ether or benzene, either when obtained directly or when first shaken with bicarbonate of soda, was an oil which did not solidify in a freezing mixture. On attempting to purify it by distillation, at 18 mm. pressure, it decomposed with effervescence, the pressure increased, and, finally, when this ceased, propionanilide distilled over, boiling at 183° at 20 mm. pressure. The decomposition possibly took place as follows:

$$C_6H_5N<{CHO \atop COCH_2CH_3} = C_6H_5N<{H \atop COCH_2CH_3} + CO$$

The oil gave propionanilide * melting at 105° when boiled with dilute sodium hydroxide.

Formylnormalbutyranilide, $C_6H_5N<{CHO \atop CO(CH_2)_2CH_3}$. — This diacid anilide was obtained only in the form of an oil and, like the preceding, it could not be solidified or distilled without decomposition. When an attempt was made to distil this crude product at 20 mm. pressure, it boiled from 164° to 185°. This fraction was distilled again at 20 mm. pressure, when the larger portion, a clear colorless oil, was collected between I72° and 180°. On standing, this fraction deposited plates, melting from 90° to 92°. The distillate was therefore a mixture of the diacid anilide with butyranilide.† The latter was obtained when the oil was boiled with dilute alcoholic sodium hydroxide.

Formylstearanilide, $C_6H_5N<{CHO \atop CO(CH_2)_{16}CH_3}$. — The stearic acid used in this experiment melted from 60° to 70°. From this the chloride was prepared according to the method of Krafft and Bürger.‡ In this case silver formanilide, suspended

* Kelbe, Ber. d. chem. Ges., xvi, 1200.

† Gerhardt, Ann. Chem. (Liebig), lxxxvii, 166.

‡ Ber. d. chem. Ges., xvii, 1380.

in ether, was used. On evaporating the ethereal solution minute, flattened, colorless crystals were obtained. These, on crystallizing repeatedly from ether, melted at 61°.

	Found.	Calculated for $C_{25}H_{41}NO_2$.
N	3.34	3.61

Formylstearanilide is extremely soluble in benzene, chloroform, ligroïn, and carbon disulphide, easily in ether, but less readily in cold alcohol. On heating the diacid anilide a decomposition takes place, as follows:

$$C_6H_5N\begin{matrix}\diagup CHO \\ \diagdown CO(CH_2)_{16}CH_3\end{matrix} = C_6H_5NC + HOCO(CH_2)_{16}CH_3.$$

When the alcoholic solution is warmed with potassium hydroxide, a bulky mass of colorless needles separates; these melt from 93° to 94°, and the product is therefore stearanilide.*

Acetylpropionanilide, $C_6H_5N<\begin{matrix}COCH_3 \\ COCH_2CH_3\end{matrix}$. — The product in this case was distilled at 18 mm. pressure, when a clear colorless oil was obtained, boiling from 159° to 160°, which did not solidify in a freezing-mixture.

	Found.	Calculated for $C_{11}H_{13}NO_2$.
N	7.46	7.33

Acetylpropionanilide is readily soluble in ether and benzene. When the analyzed substance was warmed with dilute sodium hydroxide and the product crystallized from dilute alcohol, plates of propionanilide were obtained, melting at 105°.

Acetylnormalbutyranilide, $C_6H_5N<\begin{matrix}COCH_3 \\ CO(CH_2)_2CH_3\end{matrix}$, was obtained as a clear, colorless oil, boiling at 163° under 18 mm. pressure.

	Found.	Calculated for $C_{12}H_{15}NO_2$.
N	7.18	6.83

When warmed with sodium hydroxide in alcohol, it gave butyranilide melting from 90° to 92°.

* Pebal, Ann. Chem. (Liebig), xci, 152.

Acetylisovaleranilide, $C_6H_5N<\begin{matrix}COCH_3\\COCH_2CH<\begin{matrix}CH_3\\CH_3\end{matrix}\end{matrix}$. — The isovaleryl used in this experiment boiled from 113° to 116°. The diacid anilide was an oil which was distilled at 18 mm. pressure. The fraction boiling at 161.5° to 167° was collected and redistilled at the same pressure, the larger portion then boiled between 164° and 165°.

	Found.	Calculated for $C_{13}H_{17}NO_2$.
N	6.46	6.39

The product obtained on boiling this with alcoholic sodium hydroxide was crystallized from dilute alcohol and finally from a mixture of ligroïn and benzene. It then melted at 115° and was therefore isovaleranilide.*

Acetylpalmitanilide, $C_6H_5N<\begin{matrix}COCH_3\\CO(CH_2)_{14}CH_3\end{matrix}$. — The palmitic acid used in this case melted from 61° to 62°. It was converted into the chloride according to the directions of Krafft and Bürger.† The diacid anilide was obtained as an oil, which readily solidified. It was dissolved in cold ligroïn, filtered from a small amount of acetanilide (?), and the solution was then evaporated to dryness, the residue dissolved in alcohol, and the diacid anilide precipitated with a small amount of water. It was then crystallized several times from ether, a rather unsatisfactory operation on account of its great solubility. It was thus obtained as a compact mass of colorless, indistinct, microscopic crystals, melting from 60° to 61°.

	Found.	Calculated for $C_{24}H_{39}NO_2$.
N	3.54	3.75

On warming this product with alcoholic potassium hydroxide it gave palmitanilide ‡ melting from 90° to 91°.

Experiments with Silver and Mercury Benzamide.

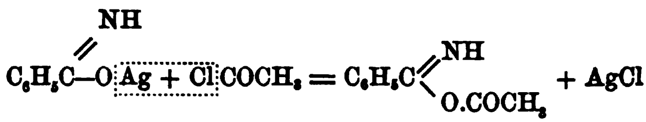
It would be expected that the silver and mercury salts of the amides would react with acid chlorides in an analogous

* Chiozza, Ann. Chem. (Liebig), lxxxiv, 109.

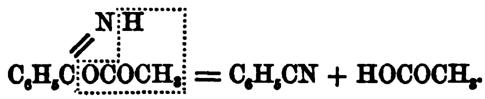
† Loc. cit.

‡ Hell and Jordanow, Ber. d. chem. Ges., xxiv, 943.

manner to the corresponding salts of the anilides, and that diacid amides would result as the chief products. This, however, is not the case with either silver or mercury benzamide. Although silver benzamide reacts with alkyl * halides precisely like silver formanilide, † *i. e.*, in both cases imido-ethers result, on the other hand, with acid chlorides, silver and mercury benzamide give chiefly benzonitrile. This reaction, in the case of the silver salts, if represented as a direct double decomposition, would be as follows:

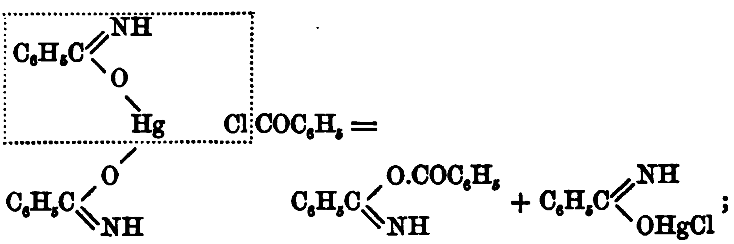


and



This apparently parallel reaction with alkyl halides would not be surprising if it were not for the entirely opposite reactions of the salts of the anilides.

In the case of the action of benzoyl chloride on mercury benzamide, using molecular proportions of the acid chloride, the yield of benzonitrile was about 72 per cent of the calculated. A direct double decomposition in this case again would be represented as follows:



* Tafel and Enoch, Ber. d. chem. Ges., xxiii, 104.
† Comstock and Kleeberg, Ibid., xii, 498.

$$\text{and } C_6H_5C\begin{cases} O.COC_6H_5 \\ NH \end{cases} = C_6H_5CN + HOCOC_6H_5.$$

While hitherto there has been no reason to assign to the salts of the amides a structure different from those of the anilides, this must now be done if the action of acid chlorides on these salts is a direct double decomposition, as shown above. For this reason these methods of representing the reactions are objectionable. It is far more probable that it is not the structure of the salts which varies in these tautomeric reactions, but that it is the mechanism of the reactions which undergoes change in different cases. It is probable in some cases that unstable addition-products * occur which break up into simpler products, and in other cases that double decompositions take place. The chief course of the reaction being influenced, not only by the union of the atoms or groups in the molecules reacting, but also by their chemical and physical nature and spacial arrangement.

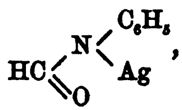
New Haven, June, 1896.

* Nef, Ann. Chem. (Liebig), cclxxxvii, 269; and Proc. Amer. Acad., May, 1892, 169.

ON THE ACTION OF ACID CHLORIDES ON THE IMIDO-ESTERS AND ISOANILIDES, AND ON THE STRUCTURE OF THE SILVER SALTS OF THE ANILIDES.*

BY H. L. WHEELER AND P. T. WALDEN.

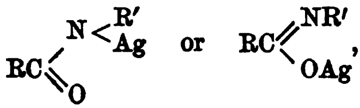
IT has been shown in recent papers † from this laboratory that the silver salts of the anilides react with acid chlorides giving diacid anilides, and, therefore, as if they had the structure



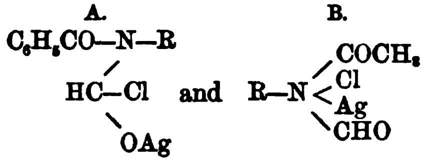
provided the action be considered as a direct replacement or double decomposition. The conclusion that follows from these reactions, with the above proviso, *i. e.*, that the silver salts have the metal joined to nitrogen, is directly opposite to that obtained by the action of alkyl halides. ‡ In the latter case it was concluded that the metal was joined to oxygen, since isoanilides or substituted imido-ethers were obtained.

These contradictory reactions are certainly not to be dismissed with the statement that they are due to tautomerism. The products obtained by acting on the silver salts with acid chlorides retained silver halide persistently, and it was considered possible that *the reaction was not a double decomposition, but that it took place first by addition then separation of silver halide.* Two forms of addition-products were considered, according to whether the silver salts are derivatives of the type

* Amer. Chem. Jour., xix, No. 2, February, 1897.
† Wheeler and Boltwood, Ibid., xviii, 381 ; Ibid., 696.
‡ Comstock and Kleeberg, Ibid., xii, 495.



, as follows:

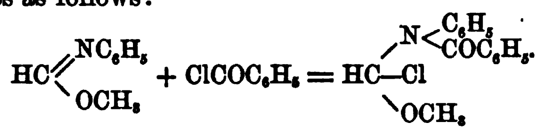


Before proceeding to the discussion of the probable structure of the silver salts, it is evidently desirable to study the action of acid chlorides on compounds that are definitely constituted according to one of the above types. The isoanilides and the free imido-esters were therefore selected with the object of determining in what manner the acid chlorides would react with compounds which undoubtedly contain the atomic grouping $RC\langle^{NR'}_{OR''}$, since this grouping is generally assumed to exist in the silver salts of the amides and anilides.

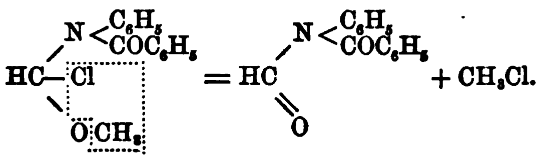
We find that the reaction takes place readily at ordinary temperatures and goes quantitatively in two ways, according to whether the imido group in the imido-ester is substituted or not.

The Action of Acid Chlorides on the Isoanilides.

The substituted imido-esters or isoanilides react with acid chlorides as follows:



This intermediate addition-product immediately decomposes with the evolution of methyl chloride, and a mixed diacid anilide results:



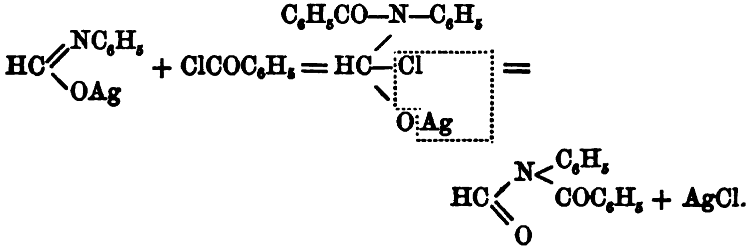
The mixed diacid anilides thus obtained decompose with alkali, giving the mono-acid anilide of the higher acid group, thus showing that they have both acid groups attached to nitrogen. That the isoanilides react so readily with acid chlorides is due to the double union between carbon and nitrogen, since, were it otherwise, the acid chloride would have to act by double decomposition on the group $-\overset{\|}{C}-OCH_3$. Such a direct double decomposition is evidently impossible, since it has been found that one of the characteristic properties of the group $-\overset{\|}{C}-OCH_3$ is that it is *not* acted on by acid chlorides. Indeed on this fact is based the general method of determining the presence or absence of this group in compounds which may contain either this or hydroxyl. In such cases, as is well known, the latter alone reacts with acid chlorides. That this reaction is not a direct double decomposition or replacement of the alkyl group by the acid radical is also shown by the fact that non-substituted imido-esters react with acid chlorides with the separation of hydrogen chloride instead of alkyl chloride (see below). It is at once evident that the only reaction which will explain the different behavior of the imido esters and isoanilides toward acid chlorides and which will be general for both cases is that of addition.

The reactions of acid chlorides on the isoanilides and imido-esters are the first that have been obtained, in the case of substances that have, or are supposed to have, the structure $RC\begin{matrix}\nearrow NR' \\ \searrow OR''\end{matrix}$, which admit of only one general interpretation, and in which the so-called tautomerism or wandering of groups is excluded. They show that the so-called tautomeric or contradictory reactions in the case of the silver salts are to be explained by addition.* We are now in a position to discuss the structure of the silver salts.

It is to be noticed that the above reactions of the isoanilides

* Compare Nef, Ann. Chem. (Liebig), cclxx, 298.

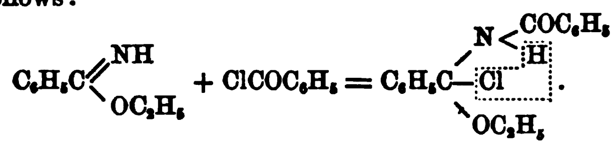
are perfectly analogous to the action of the acid chlorides on the silver salts of the anilides, and the course of the reaction in the latter case is, therefore, to be interpreted as follows, the addition taking place according to type A as given above:



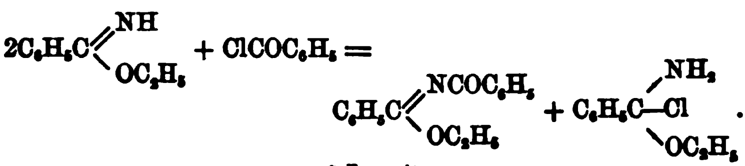
From which it follows that the silver salts of the anilides have the metal joined to oxygen as first stated by Comstock and Kleeberg.*

The Action of the Acid Chlorides on the Imido-Esters.

The non-substituted imido-esters react with acid chlorides as follows:



This intermediate addition-product, like the preceding, immediately decomposes, not however with the evolution of ethyl chloride, as in the case of the isoanilides, but by separation of hydrogen chloride. (This happens because chlorine has a greater tendency to unite with hydrogen than with methyl or alkyl.) The hydrogen chloride liberated in this manner combines with the excess of imido-ether, and the products obtained are formed as follows:



* Loc. cit.

When the acyl imido-esters are treated with acid, or when they are exposed to the air for some time, they take up a molecule of water and decompose into diacid amides as follows:

$$C_6H_5C\begin{matrix}\diagup\!\!\diagup NCOC_6H_5\\ \diagdown OC_2H_5\end{matrix} + H_2O = C_6H_5C\begin{matrix}\diagup N{-}COC_6H_5 \\ {-}OH \qquad\diagdown H \\ \diagdown O\,C_2H_5\end{matrix}.$$

The above decomposition is perfectly analogous to the action of the silver salts of the amides * and anilides† with acids, and finally this decomposition proves that the diacid amides—like the diacid anilides—have both acid groups attached to nitrogen, and the statement no longer holds true that diacid amides of the type R—CONHR, are still unknown,‡ or that in the present state of our knowledge dibenzamide may have the structure § $C_6H_5C\begin{matrix}\diagup NH\\ \diagdown OCOC_6H_5\end{matrix}$.

In fact, diacid amides of the latter type, with the acyl group attached to oxygen, are probably incapable of existence. This conclusion has been reached through the following considerations: It has been shown in a recent paper‖ from this laboratory that silver benzamide reacts with acid chlorides, giving benzonitrile, and therefore differently from the silver salts of the anilides, which give diacid anilides.¶ It has been shown above that in all probability the action of acid chlorides on silver formanilide takes place by addition. Therefore, in the case of benzamide, it must be double decomposition. (This was previously stated as the only simple explanation.) The resulting isodiacid amide is formed and breaks up as follows:

$$C_6H_5C\begin{matrix}\diagup\!\!\diagup NH\\ \diagdown OAg\end{matrix} + RCOCl = C_6H_5C\begin{matrix}\diagup N\,H\\ \diagdown OCOR\end{matrix} + AgCl.$$

* Tafel and Enoch, Ber. d. chem. Ges., xxiii, 105.

† Comstock and Clapp, Amer. Chem. Jour.. xiii, 525.

‡ Pinner, Die Imidoäther und ihre Derivate, p. 9.

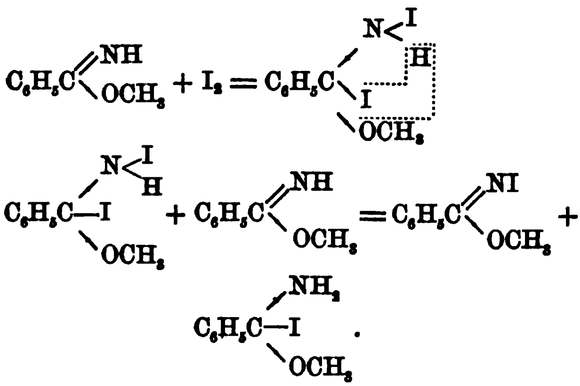
§ Pinner, Ber. d. chem. Ges., xxv, 1436.

‖ Wheeler, Amer. Chem. Jour., xviii, 701.

¶ Wheeler and Boltwood, loc. cit.

The Action of the Halogens on the Imido-Esters. Halogen Imido-Esters.

So far only the action of bromine and iodine have been tried. The result is precisely similar to that of the action of acid chlorides, two molecules of the imido-ester react with one molecule of halogen, giving halogen imido-esters and halogen hydride salts of imido-ester, most likely as follows:



Experimental Part.

Formylacetanilide, $C_6H_5N<\begin{matrix}CHO\\COCH_3\end{matrix}$.—Acetyl chloride reacts on phenylformimidoethyl ester * at ordinary temperatures with a violent evolution of ethyl chloride. It is best to modify the reaction by diluting with a dry solvent. The following procedure proved satisfactory: 5 g. of imido-ester were mixed with 5.6 g. of acetyl chloride in a mixture of ether and ligroïn. The evolution of ethyl chloride took place smoothly and a colorless oil separated. The whole was allowed to stand for twelve hours. The oil was then taken up with ether and shaken with a solution of sodium bicarbonate. On evaporating off the ether an oil was obtained which, after standing several days, was distilled at 23 mm. pressure, when practically the entire quantity distilled from 157° to 158°.

* Prepared from the silver salt of formanilide and ethyl iodide: Comstock and Kleeberg, Amer. Chem. Jour., loc. cit.

It was then cooled in a freezing-mixture and, on stirring, it solidified. After pressing on a porous plate, it was crystallized from a mixture of ether and ligroïn, when beautiful, thick, brittle crystals were obtained melting from 56° to 57°. This material proved to be identical with formylacetanilide obtained from silver formanilide and acetyl chloride.* On treating it with sodium hydrate, acetanilide was formed.

Formylbenzanilide, $C_6H_5N<\begin{matrix}CHO\\COC_6H_5\end{matrix}$. — On mixing molecular proportions of phenylformimidoethyl ester and benzoyl chloride, the reaction takes place more quietly than in the previous case. After the evolution of ethyl chloride ceases the material gives needles. When crystallized from alcohol these melt at 112°, and in other respects are identical with the products obtained from silver and mercury formanilide with benzoyl chloride. When treated with sodium hydrate it gives benzanilide. It was stated in a previous paper † that "a mixture of benzanilide and formylbenzanilide can readily be distinguished when crystallized from alcohol. The former separates first in needles; the latter forms a supersaturated solution, and on shaking deposits plates." This is a mistake, as it is just the reverse. The formylbenzanilide is the least soluble and comes down first in needles.

Formylbenzenesulphonanilide, $C_6H_5N<\begin{matrix}CHO\\SO_2C_6H_5\end{matrix}$. — Phenylformimidoethyl ester and benzene sulphochloride react slowly at ordinary temperatures. 4 g. of the imido-ether and 4.7 g. of benzene sulphochloride were mixed and kept at a temperature of about 38° to 43° for two days. The mixture then became semi-solid. It was washed with alcohol and the residue crystallized from strong alcohol, when beautiful, colorless, radiating needles were obtained. These melted at 148°–149°. This material on analysis gave the following results:

	Found.	Calculated for $C_{13}H_{11}NO_3S$.
N	5.2	5.3

* Amer. Chem. Jour., xviii, 698.
† Wheeler and Boltwood, Ibid., 381.

Half a gram of the analyzed material was boiled with a 10 per cent solution of sodium hydrate. Solution took place, and on cooling, nothing separated; dilute hydrochloric acid was then added, and the resulting colorless precipitate was washed with water and dried in the air. It melted at 110° without further purification. This was therefore benzenesulphonanilide. In the case of this mixed diacid anilide, as well as in all previous cases, alkali first removes the lower acid group.

Formylbenzorthotoluide, $CH_3C_6H_4N<\begin{matrix}CHO\\COC_6H_5\end{matrix}$. — Molecular proportions of orthotolylformimidomethyl ester and benzoyl chloride were mixed, and the whole heated to 80° until the evolution of methyl chloride had stopped. The mass was then poured into a little alcohol, when rectangular, colorless, shining plates separated. These melted at 91°, and when carefully crystallized from strong alcohol the melting-point did not change. The melting-point of this compound is therefore 91°, and not 92°, as previously stated.* It gave benzorthotoluide when treated with alkali.

Formylbenzparatoluide, $CH_3C_6H_4N<\begin{matrix}CHO\\COC_6H_5\end{matrix}$. — This was prepared from paratolylformimidomethyl ester in the same manner as the preceding compound. It was identical with the compound prepared from mercury formparatoluide and benzoyl chloride.† Its melting-point is more nearly 102° than 101°, as previously stated. When treated with alkali it gave benzparatoluide. A similar decomposition into the mono-acid anilide is slowly caused when this and the preceding compound are boiled with dilute alcohol.

Acyl Imido-Esters.

Benzoylimidoethyl Benzoate, $C_6H_5C\begin{matrix}\diagup\!\!\diagup NCOC_6H_5\\ \diagdown OC_2H_5\end{matrix}$. — When benzimidoethyl ester and benzoyl chloride ‡ are mixed (in

* Wheeler and Boltwood, Amer. Chem. Jour., xviii, 381.

† Wheeler and McFarland, Ibid., 540.

‡ The pure benzimidoethyl and methyl esters for this work were prepared according to Bushong's excellent method. Ibid., 490.

ethereal solution) in the proportion of two molecules of the former to one of the latter, and allowed to stand for twelve hours, snow-white needles separate. These consist of the hydrochloride of benzimidoethyl ester. On filtering and concentrating the ethereal solution, colorless, spear-like, or lozenge-shaped crystals separate. These were carefully crystallized from dilute alcohol for analysis. The pure material thus obtained melted at 65°.

	Found.	Calculated for $C_{16}H_{15}NO_2$.
C	76.3	75.9
H	6.1	5.9
N	5.5	5.5

Benzoylimidoethyl benzoate is stable towards alkali in the cold; acids on the other hand readily convert it into dibenzmide. When the dilute alcoholic solution is warmed with a few drops of dilute sulphuric acid, needles of the diacid amide are obtained, melting at 148°.

Acetylimidomethyl Benzoate, $C_6H_5C\genfrac{}{}{0pt}{}{/\!\!/ NCOCH_3}{\backslash OCH_3}$. — Benzimidomethyl ester and acetyl chloride, in the proportion of two molecules of the former to one of the latter, were mixed in ethereal solution. After twelve hours the hydrochloride of the imido-ester was filtered off, and on evaporating the ether an oil was obtained. This was distilled at 20 mm. pressure, when about one-third passed over below 140°, and the remainder at about this temperature. The portion boiling at 140° was redistilled at 15 mm. A few drops were removed below 139°, and then the remainder boiled almost entirely at this temperature. This fraction on cooling in a freezing-mixture did not solidify. It was analyzed with the following result:

	Found.	Calculated for $C_{10}H_{11}NO_2$.
N	8.12	7.91

The portion mentioned above, boiling below 140°, consisted of unaltered imido-ester and benzonitrile (?). When acetylimidomethyl benzoate is mixed with a little alcohol and a few drops of dilute sulphuric acid added, evolution of heat

occurs, and the whole on cooling solidifies to a mass of colorless prisms or needles. This material is acetylbenzamide, which melts at 120°.*

Acetylimidoethyl Benzoate, $C_6H_5C\begin{cases}\!/\!/NCOCH_3\\ \diagdown OC_2H_5\end{cases}$. — This was prepared from benzimidoethyl ester and acetyl chloride in the same manner as the above acyl imido-esters. The ethereal solution was washed with dilute sodium hydroxide and water. On evaporation, an oil was obtained which was distilled at 13 mm. pressure. About one-third was collected below 140.5° and the remaining two-thirds from 140.5° to 147.5°.

The larger portion was again distilled at 17 mm., when the greater part boiled at 151°. A nitrogen determination of this gave the following result:

	Found.	Calculated for $C_{11}H_{13}NO_2$.
N	7.65	7.33

When acetylimidoethyl benzoate is treated with dilute sulphuric acid, as described in the case of the methyl compound, it is converted into acetbenzamide with evolution of heat.

Halogen Imido-Esters.

The first representatives of this class of compounds in the benzoic acid series have just been prepared by Stieglitz,† who describes chlorimidoethyl benzoate and bromimidoethyl benzoate. He obtained these compounds by acting on the imido-ester hydrochlorides with sodium hypochlorite and hypobromite. These interesting compounds were obtained as oils which in the case of the chlorine compound was found to distil unchanged at 16 mm. pressure.‡

We have found that bromimidomethyl benzoate and the analogous iodimidomethyl ester result, along with other products, by directly combining the free esters with the halogen.

* Pinner, Ber. d. chem. Ges., xxv, 1436.

† Amer. Chem. Jour., xviii, 751.

‡ It is interesting to note the great stability of this substituted nitrogen chloride.

Bromimidomethyl Benzoate, $C_6H_5C\begin{smallmatrix}/\!\!/NBr \\ \diagdown OCH_3\end{smallmatrix}$. — This was obtained as a pale yellow oil of pleasant odor, which can be distilled below 20 mm. pressure. It reacts with strong aqueous ammonia with effervescence, giving off nitrogen. Dilute hydrochloric acid evolves bromine. It is therefore identical in properties with its homologue bromimidoethyl benzoate described by Stieglitz.

Iodimidomethyl Benzoate, $C_6H_5C\begin{smallmatrix}/\!\!/NI \\ \diagdown OCH_3\end{smallmatrix}$. — Iodine reacts with benzimidomethyl ester very slowly. After warming the mixture on the water-bath for several days the mass was extracted with ether, the ether shaken with solid potassium hydrate, and the uncombined iodine removed. On evaporating off the ether in a vacuum desiccator over potassium hydrate, the iodimidomethyl benzoate was obtained as a light yellow oil, mixed with unaltered imido-ester. A small amount of colorless needles separated. They were insoluble in water and boiling alcohol. They melted from 222° to 228° and were probably triphenyltricyanide or cyaphenin. When the above oil was treated with strong ammonia, it turned black from the separation of iodine. Dilute nitric acid gave the same result. On attempting to distil the crude product at 13 mm. pressure, it decomposed with the separation of iodine.

Owing to the appearance of Dr. Stieglitz's paper, and since he states his intention of further investigating these compounds, the work on the halogen imido-esters has been abandoned by us at this point. We desire to reserve the work on acyl imido-esters for ourselves, and it is our intention to investigate the action of other acid chlorides on the imido-esters and isoanilides, and also to examine the reactions of the acyl imido-esters more thoroughly.

NEW HAVEN, November, 1896.

ON THE ACTION OF CHLORCARBONIC ETHYL ESTER ON FORMANILIDE.*

BY H. L. WHEELER AND H. F. METCALF.

SIXTEEN years ago Lellmann† made the interesting observation that chlorcarbonic ethyl ester reacts energetically with formanilide, while with acet- or benzanilide no reaction was obtained, even on heating under pressure. Lellmann isolated and identified diphenylformamidine as one of the products of the reaction. He explained the formation of the amidine by stating that perhaps formylphenylurethane is formed, and that this compound appears to be quite unstable, two molecules breaking up into the amidine, carbon dioxide and ethyl oxalate.

Formylphenylurethane has been prepared by us by the action of chlorcarbonic ethyl ester on phenylimidoethyl formate or ethylisoformanilide. The reaction is precisely similar to the action of other acid chlorides on the isoanilides, and it takes place as follows: ‡

$$C_6H_5N{=}CHOC_2H_5 + ClCO_2C_2H_5 = C_6H_5NCHO.CO_2C_2H_5 + C_2H_5Cl.$$

The products being formylphenylurethane and ethyl chloride. Thus prepared, it is an oil which can be distilled with little or no decomposition. It is no more unstable than other mixed diacid anilides, and it does not suffer the above-mentioned decomposition. When warmed with acid or alkali, the formyl group is removed and phenylurethane results. It will be shown below that no ethyl oxalate is formed in the action of chlorcarbonic ethyl ester on formanilide, and that therefore Lellmann's explanation is incorrect.

* Amer. Chem. Jour., xix, No. 3.
† Ber. d. chem. Ges., xiv, 2512.
‡ Amer. Chem. Jour., xix, 129.

Just recently Freer and Sherman* have undertaken a re-examination of this reaction. They isolated the amidine, and state that in addition to this they obtained an oil which was washed with water, and which would not solidify, while "after slight warming it broke down, giving off a gas and changing to diphenylformamidine, thus showing conclusively, according to Wheeler,† that it was ethylisoformanilide, $C_6H_5N{=}CHOC_2H_5$."

If Freer and Sherman had examined the oil more carefully, which is obtained according to their directions, they would have found that it is not ethylisoformanilide. Moreover, it does not contain the slightest trace of this compound. The properties of the oil and the fact that it even partially withstood the treatment it received, show conclusively that it was not ethylisoformanilide. Ethylisoformanilide or phenylimido-ethyl formate was first obtained by Comstock and Clapp.‡ These authors describe it, as stated in Beilstein's Handbuch,§ as an oil boiling from 213° to 215° at 741 mm. pressure.‖ In the article to which Freer and Sherman refer this imido-ester was not described as an oil which decomposes on distillation, but which boils at 18 mm. pressure at about 106°. Under these conditions it has therefore almost the same boiling-point as its isomeric imido-ester, *i. e.*, imido ethyl benzoate.¶

Ethylisoformanilide and all the other isoanilides prepared in this laboratory** differ from the imido-esters of Pinner, inasmuch as they cannot be washed with water without decomposition; indeed, on exposure to the moisture of the air, they soon solidify, changing into the corresponding amidines, or regenerating the formyl compound. The peculiar penetrating pleasant odor of the isoanilides, like that of the imido-esters of Pinner, is characteristic, and traces of these compounds can readily be detected by their odor. This odor was entirely lacking in the above-mentioned oil.

* Amer. Chem. Jour., xviii, 579.
† Ibid., xviii, 381.
‡ Ibid., xiii, 527.
§ Dritte Auflage, p. 359.
‖ Compare also Claisen, Ann. Chem. (Liebig), cclxxxvii, 364.
¶ Bushong, Amer. Chem. Jour., xviii, 490.
** Ibid., xii, 499; xiii, 515, 525.

If ethylisoformanilide is formed in the action of chlorcarbonic ester on formanilide, which most probably is the first step of the reaction, its existence would naturally be very brief in the presence of chlorcarbonic ester, and, as shown in this paper, it would further react, not only with the chlorcarbonic ester, giving formylphenylurethane, but also probably with hydrogen chloride and the water, which are formed as by-products.

From this and the following it will be seen that hitherto the only products which have been accurately identified in this reaction are diphenylformamidine hydrochloride and carbon dioxide. By a more thorough examination of this reaction we have obtained the following as final reaction-products: Diphenylformamidine hydrochloride, formylphenylurethane phenylurethane, carbon dioxide, carbon monoxide, and ethyl chloride, and the oil which Freer and Sherman state is ethylisoformanilide will be shown in the experimental part of this paper to be a mixture of the nitrogen derivative formphenylurethane, phenylurethane, and any unaltered formanilide. It must also have contained some chlorcarbonic ester when they attempted the distillation. It frequently has a slight odor resembling monochlorethylacetate, which possibly comes from a slight impurity in the carbonic ester. At any rate the quantity of this material is extremely small.

The formation of the above products would seem to indicate that formanilide and silver formanilide react with chlorcarbonic ethyl ester in the same manner, except that in the case of formanilide the reaction is complicated by the secondary reactions of hydrogen chloride. The products in these two reactions are identical, so that one general equation may represent the primary reaction as follows:

$$HC\left\langle\begin{matrix} NC_6H_5 \\ O\boxed{R + Cl}CO_2C_2H_5 \end{matrix}\right. = HC\left\langle\begin{matrix} NC_6H_5 \\ O\boxed{CO_2}C_2H_5 \end{matrix}\right. + RCl,$$

the unstable isodiacid anilide thus formed separating carbon dioxide, which is frequently the case with chlorcarbonic ester

reactions, giving phenylimidoethyl formate. Here, however, it has only a brief existence, as it immediately reacts with the chlorcarbonic ester, giving formylphenylurethane and ethyl chloride as follows: *

$$HC\begin{cases}=NC_6H_5\\ -OC_2H_5\end{cases} + ClCO_2C_2H_5 = HC\begin{cases}-N<\begin{matrix}C_6H_5\\ CO_2C_2H_5\end{matrix}\\ -\boxed{Cl}\\ -O\ \boxed{C_2H_5}\end{cases}.$$

On the other hand, the ingenious suggestion of Freer and Sherman to account for the formation of ethylisoformanilide, may represent the primary course of the reaction if formanilide has the structure $HC\begin{cases}-NHC_6H_5\\ =O\end{cases}$. They assume that the chlorcarbonic ethyl ester adds on the nitrogen, which then becomes pentavalent, and the addition-product thus formed decomposes into the imido-ester, carbon dioxide, and hydrogen chloride. It is to be noticed that if the reaction takes place in this manner, it is analogous to the action of other acid chlorides on the anilides, at least in regard to the formation of an intermediate pentavalent nitrogen addition-product.†

At any rate, there is little doubt that phenylimidoethyl formate is the first product of the reaction. Wallach ‡ has shown that hydrogen chloride converts formanilide into diphenylformamidine hydrochloride, possibly as follows:

$$2C_6H_5NHCHO = C_{13}H_{12}N_2HCl + CO + H_2O.$$

This and the fact that the isoanilides are converted into amidines by hydrogen chloride § accounts for the formation of carbon monoxide and the amidine hydrochloride in the above reaction. The formation of carbon monoxide may also be due to the displacement of the formyl group, as formyl chloride, which decomposes into the oxide and hydrogen chloride.‖

* In the case of the silver salt a small amount of ethylisoformanilide was actually isolated. It is therefore evident that the chlorcarbonic ester has a greater tendency to react with the silver salt than with the isoanilide, while in the case of formanilide the facts are the reverse.

† Pictet, Ber. d. chem. Ges., xxiii, 3015. ‡ Ibid., xv, 208.

§ Comstock and Kleeberg, Amer. Chem. Jour., xii, 493.

‖ Compare Pictet, loc. cit.

Formylphenylurethane may be a secondary product, and result from the action of the chlorcarbonic ester on the isoanilide first formed, or it may be a primary product, as follows:

$$HC\begin{matrix} /\!\!/ NC_6H_5 \\ \diagdown OH \end{matrix} + ClCO_2C_2H_5 = HC\begin{matrix} \diagup N{<}\begin{matrix} C_6H_5 \\ CO_2C_2H_5 \end{matrix} \\ -\boxed{Cl} \\ \diagdown O\boxed{H} \end{matrix}$$

its formation then being analogous to that of the diacid anilides from the silver salts * and from the isoanilides.† Phenylurethane naturally results from formylphenylurethane, since all mixed diacid anilides, by treatment with acids, first liberate the lower acid radical.

Thus it will be seen that the formation of all the products of the action of chlorcarbonic ethyl ester on formanilide can readily be explained whether formanilide, as its name implies, is an anilide with the structure $HCO.NHC_6H_5$, or whether it has the imido structure and is phenylimidoformic acid. Its structure cannot, therefore, be determined by the final reaction-products in this case, but the analogy which this reaction shows with that of the silver salt is strongly in favor of the imido formula.

The recent work bearing on the structure of formanilide appears to favor the view that this compound is an imido acid. Cohen and Archdeacon ‡ conclude, from their interesting work on sodium alcoholate addition-products of the anilides, that the structure of formanilide, and indeed also of other anilides, is best represented by the imido formula.

Claisen, § on the other hand, has recently given what at first sight appears to be a strong argument for the amide structure, *i. e.*, that the sodium salts of the true oxymethylene compound, oxymethylene camphor, for example, give O-esters with ethyl iodide, while formanilide does not. He carries, however, this analogy, or lack of analogy, too far when he states that if formanilide has the structure $C_6H_5N{=}CHOH$,

* Wheeler and Boltwood, Amer. Chem. Jour., xviii, 381.

† Wheeler and Walden, Ibid., xix, 129.

‡ Jour. Chem. Soc. (1896), 91. § Ann. Chem. (Liebig), cclxxxvii, 360.

it should boil lower than its O-ethyl derivative, $C_6H_5N=CHOC_2H_5$, while the fact is that formanilide boils higher.

He arrived at this conclusion from a consideration of the boiling-points of the following compounds:

	B. P.		B. P.
Oxymethylene camphor,	251°	O-Ethyl derivative,	270°
Oxymethylene-acetoacetic ester,	200°	O-Ethyl derivative,	266°
Oxymethylene-acetylacetone,	190°–200°	O-Ethyl derivative,	257°

The objection to this reasoning is that the above compounds do not contain the nitrogen-carbon grouping $-N=CHOH$ in question, but the carbon-carbon grouping $=C=CHOH$, which is assumed to be analogous without sufficient reason. For it might be argued that compounds containing the nitrogen-carbon grouping $-N=CHOH$ would show differences in the boiling-points similar to those containing the oxygen-carbon grouping $O=CHOH$, that is, that the imido-acids and their esters would be expected to correspond with the simple acids and their esters, and, since the acids boil higher than their esters and formanilide higher than its ester, the structure $C_6H_5N=CHOH$ is the correct one for formanilide.

For example:

	B. P.		B.P.
$O=CHOH$,	99°	$O=CHOC_2H_5$,	54°.4
$O=C(CH_3)OH$,	118°	$O=C(CH_3)OC_2H_5$,	77°
$O=C(C_6H_5)OH$,	250°	$O=C(C_6H_5)OC_2H_5$	213°
$C_6H_5N=CHOH$,	294°	$C_6H_5N=CHOC_2H_5$,	212°

Similar reasoning to that which has led Claisen to consider formanilide as an anilide may be employed to show that it is not. For if instead of drawing conclusions in regard to its structure from comparison of compounds containing the group $=C=CHOH$ with their ethyl esters, a comparison is made of compounds containing the group $\equiv C-CHO$, with what theoretically would be their O-derivatives, we find that the compounds with the true formyl group, in this case also, boil lower than the O-ethyl derivatives. Therefore, since the boiling-point of formanilide does not correspond with this series, formanilide must have the imido structure.

For example:

	B. P.		B. P.
$H_3C—CHO$,	20°.8	$H_2C=CHO—C_2H_5$,	35°.5
$(CH_3)_2CO—CHO$,	63°	$(CH_3)_2C=CHOC_2H_5$,	92°-94°
$CH_3(C_2H_5)CH—CHO$,	90°	$CH_3(C_2H_5)C=CHOC_2H_5$,	111°
$C_6H_5NH—CHO$,	294°	$C_6H_5N=CHOC_2H_5$,	212°

This shows that there is no analogy to be expected between the boiling-points of oxymethylene derivatives containing the group $=C=CHOH$ with formanilide. On account of the relation which exists between the boiling-points of acids and their esters, and since formanilide or phenylimidoformic acid and its ester show this same relation, the conclusion to be drawn (if any) from the boiling-points is that formanilide has the imido structure.

Although the group $—N=CHOH$ may exist in formanilide, it cannot exist in the secondary anilides, that is, in such compounds as methyl formanilide, or in the diacid anilides, benzoyl formanilide, for example. These compounds must have the structure,

$$C_6H_5N{<}\begin{matrix}\overset{H}{\overset{|}{C}}{=}O\\ CH_3\end{matrix} \quad \text{and} \quad C_6H_5N{<}\begin{matrix}\overset{H}{\overset{|}{C}}{=}O\\ COC_6H_5\end{matrix}.$$

Auwers * has found that formanilide shows in its cryoscopic behavior a departure from the formyl secondary anilides. This, as Auwers states, may be due to some unknown cause, and not necessarily result from the presence of hydroxyl in formanilide.

It is interesting also to note that formanilide, as first shown by Comstock and Kleeberg, readily forms a silver salt, while acet- and benzanilide apparently do not. It may be stated in general that formanilide is far more reactive than the other anilides. These facts would seem to indicate that formanilide has the imido structure, and therefore reacts with chlorcarbonic ethyl ester in the manner first stated above.

* Zeitschr. phys. Chem., xii, 711; xv, 48, 49.

Experimental Part.

ACTION OF CHLORCARBONIC ETHYL ESTER ON FORMANILIDE.

On mixing chlorcarbonic ethyl ester and formanilide, an absorption of heat takes place, the formanilide slowly dissolves, and, at 23°, a slow evolution of gas soon takes place. At 60° to 70° the evolution of gas is rapid, while on the water-bath it may become violent, as Lellmann observed.

The Liquid and Solid Products.—60 g. of formanilide and 54 g. of chlorcarbonic ethyl ester were mixed and warmed until solution took place, and the reaction was well started. After a short time the material was placed in a desiccator over lime until the odor of the ester had disappeared. It was then taken up in ether and separated from the diphenylformamidine hydrochloride which remained. This residue was dissolved in water and precipitated by ammonia, when it melted at about 136°. The ethereal solution was washed with water, until all the amidine salt was removed; it was then dried over calcium chloride and the ether evaporated. This then gave the oil which has been supposed to contain ethyl oxalate and ethylisoformanilide. A portion of this was shaken with strong ammonia; it then showed no signs of alteration and no oxamide was obtained. Ethyl oxalate could not, therefore, have been present. Another portion was shaken with dilute hydrochloric acid; the remaining *oil* was extracted with ether and the aqueous acid solution was then found to contain nothing but a trace of aniline hydrochloride. Since no amidine was formed by this treatment, the absence of ethylisoformanilide in this oil is established. The remaining portion of the oil, which had not been treated with ammonia or acid, and which had a slight odor resembling monochlorethyl acetate, but none resembling ethylisoformanilide, was then subjected to distillation. Unsuccessful attempts were previously made to solidify this oil by freezing. On distilling, it all boiled over at 14 mm. pressure from 159° to 165° without showing any signs of decomposition, at least the amount of gas given off, as stated by Freer and Sherman,

was so insignificant that the pressure remained constant during the entire distillation. The residue was also insignificant and diphenylformamidine was not formed. The oil was again distilled at 15 mm. pressure. It then boiled for the greater part from 162° to 164°. On further distilling it showed signs of decomposition, the boiling-point rose to 170°, and in the receiver a trace of a sharp odor, probably of phenyl isocyanate, was noticed. The distillate remained as an oil on cooling. It was then boiled with sodium hydroxide in dilute alcoholic solution, in order to decompose formylphenylurethane into phenylurethane. On cooling, an oil separated, which when treated with dilute hydrochloric acid solidified in a freezing mixture. On crystallizing this material from dilute alcohol, it melted at 52°, and in all its properties was identical with phenylurethane.

Phenylurethane is one of those substances which when melted, or when separated from an alcoholic solution, may remain liquid for a long time. Formanilide also belongs to this class of substances which when impure are difficult to solidify, while formylphenylurethane is an oil. Mixtures of the above substances would not therefore be expected to completely solidify or readily to deposit crystals on cooling.

In another experiment where the action was more complete and no formanilide was apparently present, a portion of the oil did solidify on cooling, and this was found to be phenylurethane. On boiling the whole with sodium hydroxide, and then cooling, it apparently solidified completely, giving only the urethane. This shows that the oil was undoubtedly mostly formylphenylurethane, and the oil which Freer and Sherman obtained must have contained the above-mentioned substances along with some chlorcarbonic ester, since they state that on warming it gave off a gas, and they obtained more amidine, that is, in their case, the reaction was not completed at first.

In another experiment, using two molecules of formanilide to one of chlorcarbonic ethyl ester, the products were the same. Hence, naturally, the oil contained a large amount of

formanilide. The greater portion of this was separated by concentrating the ethereal solution, when the formanilide separated as an oil, which on standing crystallized. The ethereal filtrate from this gave an oil which boiled, for the most part, at 14 mm. pressure from 147° to 151°. The observed boiling-point of formylphenylurethane in the same apparatus at 15 mm. pressure was 149° to 151°, while phenylurethane boiled at 151°, and formanilide at 165° to 166°. Since in the above reaction hydrogen chloride is formed, and this converts the formylphenylurethane into phenylurethane, the oil is therefore always a mixture of these compounds, and it contains in addition any unaltered formanilide. Since the boiling-points of these substances lie so close together, attempts to isolate formylphenylurethane, free from admixture, in this case were abandoned. The oil was then converted into the urethane by boiling with sodium hydroxide, and the product thus obtained was a mixture of urethane and formanilide.

Formanilide and phenylurethane in the absence of formylphenylurethane, *i. e.*, after boiling with sodium hydroxide, etc., can readily be separated. When such a mixture is crystallized from quite dilute alcohol, formanilide first separates, while when the mixture is treated with ligroïn it is the phenylurethane that is extracted.

A better yield of the oil can be obtained by carrying out the reaction in benzene.

The Gaseous Products. — The gases were collected over water and examined as follows: The carbonic acid and ethyl chloride were removed together with cold dilute solution of sodium hydrate; the presence of carbon dioxide was then shown in the usual way. On warming this solution ethyl chloride was given off. This burned with a greenish flame, and was shown to contain chlorine by passing the gas over heated calcium oxide, dissolving in nitric acid and precipitating with silver nitrate. Separate experiments under the same conditions with chlorcarbonic ester and boiling sodium hydrate gave no burnable gas. Carbon dioxide and ethyl chloride are the chief constituents of the gaseous products. After the

sodium hydrate solution and then cold water failed to diminish the volume of gas, a cuprous chloride solution in hydrochloric acid was run into the burette. This absorbed the greater part of the remaining gas, thus showing the presence of carbon monoxide; the comparatively small part not absorbed was air which had accidentally entered in handling the products.

The results of the above experiments serve to identify the following compounds: Diphenylformamidine hydrochloride, formylphenylurethane, phenylurethane, carbon dioxide, carbon monoxide, and ethyl chloride.

Formylphenylurethane, $C_6H_5N<\begin{matrix}CHO\\CO_2C_2H_5\end{matrix}$.—This diacid ester anilide was not obtained free from formanilide or phenylurethane when chlorcarbonic ethyl ester acted on formanilide. It can be obtained pure, however, from ethylisoformanilide and chlorcarbonic ethyl ester as follows:

Sixteen g. of ethylisoformanilide were treated with a slight excess over one molecule of the ester; a lively reaction took place (requiring the use of a return-condenser). Heat was evolved and a stream of ethyl chloride escaped. The reaction was complete in a short time. The whole was then placed over lime in a desiccator until the odor of chlorcarbonic ester disappeared. It was then distilled, and after fractioning, a portion was obtained boiling from 149° to 151° at 15 mm. pressure. This did not solidify on cooling, and on analysis the following results were obtained:

	Found.	Calculated for $C_{10}H_{11}NO_3$.
C	62.67	62.18
H	5.98	5.69
N	7.55	7.23

When the analyzed material was boiled with alkali, it decomposed with the separation of the lower acid group, giving phenylurethane. When it was mixed with phenylhydrazine, it soon solidified; the solid was washed with ether, and this then left pure *α*-formylphenylhydrazine, melting at 140°. These results show that formylphenylurethane has the structure above assigned to it, both acid groups being attached to nitrogen.

NEW HAVEN, December, 1896.

ON THE PREPARATION OF METABROMBENZOIC ACID AND OF METABROMNITROBENZENE.*

BY H. L. WHEELER AND B. W. McFARLAND.

IT is now over thirty years since Reinecke † showed that benzoic acid could be directly brominated. His method was to heat the acid with bromine and water, in a closed tube, to 100° for several days. Reinecke's method, with the modifications of Hübner, Ohly, Philipp,‡ Petermann,§ and Angerstein ‖ for its purification, is given in the last edition of Beilstein's *Handbuch* as the method of preparation ("Darstellung").

Again, according to the above authority, metabromnitrobenzene is best prepared as follows (*i. e.*, "Darstellung"): "Man erhitzt in Röhren von 150 c.c. Inhalt je 35 g. Nitrobenzol mit 32.5 g. (über H_2SO_4 entwässertem) Brom und 1 g. pulverisirten Eisenchlorid zwölf Stunden lang auf 60°–70°." This is Scheufelen's ¶ method, and it gives a yield of over 80 per cent of the calculated quantity of pure metabromnitrobenzene.

Scheufelen also showed that ferrous bromide would readily effect the bromination in closed tubes. An experiment of his in an open vessel was not a success, however, since only 25 per cent of the theoretical yield of metabromnitrobenzene was obtained.

The above methods can be greatly simplified, inasmuch as the operations can be performed in a short time and without the use of closed tubes if iron be used as a bromine carrier.

* Amer. Chem. Jour., xix, No. 5.
† Zeitschr. Chem., 1865, 116; 1869, 109.
‡ Ann. Chem. (Liebig), cxliii, 283.
§ Ibid., cxlix, 131.
‖ Ibid., clviii, 5.
¶ Ibid., ccxxxi, 165.

Moreover, contrary to the result of Scheufelen, a yield of metabromnitrobenzene almost equal to that obtained in closed tubes with ferrous bromide, can be obtained in open vessels by the use of iron.

Iron, as a bromine-carrier, is now frequently used in other cases, since it often effects bromination with surprising readiness. This property of iron is well illustrated with paradichlorbenzene. (See below.) From the experiments with iron and ferrous bromide, in the case of nitrobenzene, it appears that iron is a better carrier of bromine than separately prepared ferrous bromide, and naturally more convenient.

Metabrombenzoic Acid. — After a number of experiments we have come to the conclusion that the following is the best method for the preparation of this acid: 20 g. of benzoic acid and 6 g. of iron wire or gauze are placed together in a flask connected with a condenser and heated on a metal bath. When the temperature of the bath reaches about 170° 48 g. of bromine are added, drop by drop, while the temperature of the bath is allowed to rise until at the end of the operation it reaches 260°. The addition of the bromine requires about one hour and a half, with the above quantities, when the bromination is finished. The quantity of bromine given is sufficient to convert all the iron into ferrous bromide, the benzoic acid into monobrombenzoic acid, and then allow 4.7 g. for loss. Generally, however, not all the iron is attacked and some dibrombenzoic acid results.

After the bromine has been added the mass is dissolved in sodium hydroxide, filtered from the iron and ferric hydroxide, and after precipitating the metabrombenzoic acid with hydrochloric acid it can then be purified in the usual way. We proceeded as follows in the purification: After precipitating the acid with hydrochloric acid it was shaken out with ether. This gave a crude product weighing 32 g.; calculated weight for monobrombenzoic acid, 32.9 g. This was distilled, and the portion boiling below 300° (none came over below 280°), and weighing 20 g., was crystallized once from 50 per cent alcohol. It melted from 145° to 148° and was

therefore practically pure metabrombenzoic acid. From this it will be seen that the yield of the acid does not lie far short of being equal to the weight of benzoic acid employed. The same material crystallized three times from benzene melted at 152°–153°, which is the melting-point usually assigned to the pure acid.*

Perbrombenzene, C_6Br_6.—An experiment in a closed tube gave perbrombenzene as the sole product. The carboxyl group of the acid being displaced, 5 g. of benzoic acid, 2 g. of iron, and 37.4 g. of bromine were heated in a tube to 225° for five hours. On opening the tube great pressure was observed and the bromine had entirely disappeared. The crystalline product obtained was difficultly soluble in the ordinary solvents; from benzene it separated in the form of needles and did not melt below the boiling-point of sulphuric acid.

Metabromnitrobenzene.—30 g. of nitrobenzene and 3 g. of iron wire are placed in a flask with reversed condenser and heated up to 120° in an oil-bath. 60 g. of bromine are then gradually added, the operation taking about three-quarters of an hour. The flask is left in the bath for three-quarters of an hour more, and then the contents distilled in steam. The crude, almost pure, product thus obtained after pressing on paper and drying amounts generally to about 75 per cent of the calculated. We have obtained a yield, however, as high as 85 per cent by the above method. In one experiment using three times the above quantities a yield of 64 per cent of the calculated was obtained. These results, although somewhat lower than the best obtained in closed

* Metabrombenzoic acid resembles benzoic acid in the manner in which its melting-point is lowered by a slight amount of impurity or admixture. Friedburg (Ann. Chem. (Liebig), clviii, 23) states that the pure acid melts at 155°, and that benzoic acid melts at 121°, while a mixture of these acids containing 20 per cent of benzoic acid melts as low as 115°, and therefore 6° lower than benzoic acid. With larger amounts of impurities the melting-point of the mixture was observed as low as 96°, and, as Friedburg states: "Man sieht also, das man sich nicht wundern darf, bei der Bereitung der Brombenzoesäure niedrig schmelzende Gemische zu erhalten."

tubes, are highly satisfactory when one considers the greater time required and the other disadvantage in the closed-tube method.

1,4-Dichor-2,5-Dibrombenzene (?). — An experiment with paradichlorbenzene was interesting as a further illustration of the ease with which iron often effects bromination. Paradichlorbenzene, when pure, can be boiled with its own volume of bromine and the bromine all driven off without altering its melting-point or without its giving off hydrogen bromide. If, however, a piece of iron be added to the warmed mixture, a strong effervescence takes place, hydrogen bromide is given off, and the reaction proceeds of itself, the product soon solidifying. After pulverizing and washing out the iron bromide, the residue can be crystallized from hot absolute alcohol, in which it is difficultly soluble. It then gives beautiful colorless needles or prisms which melt at about 148°. A product thus obtained gave the following results on analysis:

	Found.	Calculated for $C_6H_2Cl_2Br_2$.
Cl	23.26	23.31
Br	52.33	52.46

This is presumably 1, 4-dichlor-2, 5-dibrombenzene, the corresponding tetrabrombenzene which it resembles in regard to solubility, etc., being also formed by direct bromination. With the exception of the fact that it was found that this compound is very unreactive, it was not further investigated, test-tube experiments showing that it was not affected appreciably by boiling with nitric acid, and that it could be volatilized from fused sodium hydrate.

In conclusion, the authors desire to express their thanks to Messrs. W. M. Bradley, G. R. Tracy, and W. Valentine, who have assisted in the present work.

New Haven, February, 1897.

ON THE NON-EXISTENCE OF FOUR METHENYL-PHENYLPARATOLYLAMIDINES.*

BY H. L. WHEELER.

IN the first number of the Journal für praktische Chemie for this year, Walther † describes the preparation of methenylphenylparatolylamidine by four different methods. Each method, according to him, gave a new amidine, and these amidines were supposed to be isomers. The methods he used and the compounds he claims to have obtained are as follows:

I. By heating methenyldiphenylamidine with *p*-toluidine a product was obtained which melted at 120°. He explains the formation of this as follows:

$$HC\left\langle\begin{matrix} NC_6H_5 \\ \boxed{NHC_6H_5 \quad H}NHC_6H_4CH_3 \end{matrix}\right. \rightarrow HC\left\langle\begin{matrix} NC_6H_5 \\ NHC_6H_4CH_3 \end{matrix}\right. .$$

II. By boiling an alcoholic solution of methenyldiparatolylamidine with aniline hydrochloride, a product melting at 132° was obtained:

$$HC\left\langle\begin{matrix} NC_6H_4CH_3 \\ \boxed{NHC_6H_4CH_3 + H}NHC_6H_5.HCl \end{matrix}\right. =$$

$$HC\left\langle\begin{matrix} NC_6H_4CH_3 \\ NHC_6H_5 \end{matrix}\right. .HCl + H_2NC_6H_4CH_3.$$

III. By treating a mixture of *p*-formtoluide with aniline and phosphorus trichloride a product melting at 98° was obtained. He states that the following amidine is expected to result here:

$$HC\left\langle\begin{matrix} NHC_6H_4CH_3 \\ \boxed{Cl_2 + H_2}NC_6H_5 \end{matrix}\right. \rightarrow HC\left\langle\begin{matrix} NHC_6H_4CH_3 \\ NC_6H_5 \end{matrix}\right. .$$

* Amer. Chem. Jour., xix, No. 5.

† Bd. lv, 41.

IV. Finally, he states that by reversing the above and treating a mixture of formanilide and *p*-toluidine with phosphorus trichloride a reaction as follows must take place, or, in other words, that an amidine with the following structure must result:

$$HC\left\langle\begin{matrix}NHC_6H_5\\ \boxed{Cl_2 + H_2}NC_6H_4CH_3\end{matrix}\right. \rightarrow HC\left\langle\begin{matrix}NHC_6H_5\\ NC_6H_4CH_3\end{matrix}\right. .$$

Walther concludes that two of these amidines are structural isomers while the others are perhaps physical modifications or stereochemical isomers.

The existence of four isomeric methenylphenylparatolylamidines is theoretically possible, and would therefore not be remarkable, but that these four should be formed separately in the above reactions is not in harmony with the general behavior of amidines, imide chlorides,* or imido-esters, and that these substances should act by direct double decomposition, as indicated above, seems incredible. Moreover, these results are not in harmony with the careful work of Pechmann † on the amidines. Pechmann has shown in several cases that only one amidine results, when prepared from imide chlorides, where two might be expected.‡

The re-examination of the above products was therefore undertaken with the result that all attempts to confirm the statements of Walther were unsuccessful. In no case, by the first and second method, were products obtained that melted constantly at 120° or 132°. Products were obtained that

* Most probably imide chlorides are to be considered in reactions III and IV and not amide chlorides.

† Ber. d. chem. Ges., xxviii, 869 and 2362.

‡ It may be stated here that seven years ago, while the author was engaged in a research on the isoanilides with Mr. W. J. Comstock, it was observed that the same amidine resulted when prepared from phenylformimidomethyl ester and metanitraniline or from metanitrophenylformimidomethyl ester and aniline. The products obtained by these different methods were identical in regard to melting-point and general behavior. The preparation of this amidine by only one method was given at that time, the intention being to examine the subject more thoroughly, and the work had just been resumed when Pechmann's article appeared.

melted near these temperatures, and corresponded otherwise with Walther's descriptions, but, when crystallized, they proved to be nothing but impure methenyldiphenylamidine and methenyldiparatolylamidine, respectively.

According to the third and fourth method apparently one and the same methenylphenylparatolylamidine was obtained. This did not melt at 98° nor at 102° when purified by repeated crystallizations, but more nearly at 103.5° to 104°, when prepared by the third method, and at 103.5° to 104.5°, or practically at 104°, when prepared by the fourth method. The products could not be distinguished in appearance and properties except by this slight difference in melting-points. This difference in complete melting is to be explained by the fact that when this amidine is prepared by the third method, under certain conditions, an impurity accompanies the chief product, which it is difficult or impossible to separate by crystallizing from ligroïn. This impurity is probably methenyldiparatolylamidine.

The amidine at about 103.5° is the true methenylphenylparatolylamidine, since the same compound results from paratolylformimidomethyl ester and aniline.

Walther comments on the products obtained by the third and fourth methods, as follows: "Allein an der Verschiedenheit beider Körper ist nicht zu zweifeln; beim Umkrystallisiren derselben aus warmem Petroläther ist der Unterschied in ihrem Verhalten schon deutlich ausgeprägt: der Körper vom Schmelzp. 98° löst sich leichter und fält beim Abkühlen der Lösung sofort in weissen Nadeln aus, der Körper von Schmelzp. 102° geht schwerer in Lösung und setzt sich langsam in harten kleinen Prismen ab."

The products that I obtained by Walther's third and fourth methods could be made to crystallize at will in the form of needles or prisms. In order to obtain the needle form, a strong ligroïn or petroleum ether solution is taken, and cooled rapidly. If the solutions are dilute or moderately dilute, and are slowly cooled, or if allowed to evaporate spontaneously, prisms are invariably obtained. Apparently the

prisms are obtained more readily the purer the material. No difference in melting-point was observed between the needles and prisms when these forms were prepared from pure material. The difference in solubility of these forms is only apparent; the prisms are thicker, larger crystals, and therefore, of course, dissolve less *rapidly* than the finely divided slender needles.

Platinum double salts of the supposed new amidines were obtained by Walther in each case, but since these were obtained from impure material, nothing would be gained by examining these. Attention was directed therefore entirely to the amidines.

The formation of only one amidine in reactions III and IV shows that the reaction is not a direct double decomposition, but that it involves an addition and then a separation. For example, both imide chlorides formed from the formyl compounds add the base giving the same compound, *i. e.*, the hydrochloric acid salt of the amidine, and this naturally breaks down in one way, or chiefly in one way:

$$\left.\begin{array}{l} HC\begin{cases}=NC_6H_4CH_3\\ -Cl\end{cases} + H_2NC_6H_5 \\ HC\begin{cases}-Cl\\ =NC_6H_5\end{cases} + H_2NC_6H_4CH_3\end{array}\right\} \rightarrow HC\begin{cases}-NHC_6H_4CH_3\\ -Cl\\ -NHC_6H_5\end{cases}$$

The above addition-product can separate hydrogen chloride in either of two ways according as the double bond in the free amidine is between the methenyl group and the aniline or the toluidine rest. These reactions, therefore, show nothing in regard to the structure of methenylphenylparatolylamidine.

The Product Obtained by the First Method.

The directions for the preparation of the amidine melting at 120° are somewhat indefinite. Walther states: "Wird Diphenylmethenylamidin mit 1 mol. freien *p*-Toluidins längere zeit erhitzt, so erhält man eine Abscheidung von Anilin. Das resultirende gemischte Amiden bildet shöne weisse Nadeln von Schmelzp. 120°."

No temperatures are given, nor is the solvent stated which was used in the purification (?) of the product. Attempts to prepare this amidine were made as follows: 1.2 g. methenyldiphenylamidine and 0.6 g. of paratoluidine were heated to 100° for about three days. The material on cooling then became a dark-colored semi-solid mass. It was dissolved in cold alcohol and precipitated with water, dried on a plate, and then crystallized from ligroïn. It separated finally in the form of white needles, as Walther states, but the different crystallizations melted about as follows:

I.	102°–110°	IV.	125°–127°	VII.	131°–133°
II.	117°	V.	127°–129°	VIII.	131°–133°
III.	120°–125°	VI.	128°–131°		

In the next experiment a larger quantity of material was taken. 5.5 g. of methenyldiphenylamidine and 3.0 g. of paratoluidine were kept at about 80° for four days and nights. The black mass was then taken up in alcohol precipitated with water, dried, and boiled in ligroïn with animal charcoal. On crystallizing from ligroïn needles separated, and the following melting-points were obtained:

I.	100°–108°	IV.	121°–125°	VII.	135°–136°
II.	112°–115°	V.	125°–129°	VIII.	135°–136°
III.	115°–122°	VI.	130°–132°		

The above results show that the product thus obtained is a mixture, and that the amidine crystallizing in white needles, as described by Walther, is undoubtedly impure methenyldiphenylamidine. The melting-point of this is given by various observers from 135° to 140°. Other solvents besides ligroïn were tried, but no amidine melting constantly at 120° was obtained. The product was readily soluble in alcohol, ether, carbon disulphide, benzene, and chloroform. It had the appearance and properties of methenyldiphenylamidine.

The Product Obtained by the Second Method.

According to the second method, by heating methenyldiparatolylamidine* with aniline hydrochloride for a half hour in alcoholic solution, an amidine melting at 132° should result. The solvent used in purifying is not stated.

An experiment to confirm this statement was undertaken as follows: 2.9 g. of methenyldiparatolylamidine and 1.7 g. of aniline hydrochloride were warmed in a small amount of alcohol for a half hour on the steam-bath. (If warmed for a longer time the amidine is decomposed and nothing separates.) On cooling, a mass of needles separated. These were dissolved in alcohol and precipitated with dilute ammonia, dried, and crystallized repeatedly from ligroïn. The products from the successive crystallizations gave approximately the following melting-points:

I.	125°	IV.	133°–137°	VII.	137°–140°
II.	132°	V.	135°–138°		
III.	132°–136°	VI.	137°–140°		

A portion of the hydrochloride was crystallized four times from alcohol and then decomposed with ammonia. Thus obtained it melted at about 135°–136°. When the crude amidine was crystallized twice from absolute alcohol, in which it is quite soluble, it melted at 132°–135°.

In another experiment 5 g. of the amidine and 3 g. of aniline hydrochloride were taken. The hydrochloric acid salt resulting on warming this mixture was crystallized six times from absolute alcohol and then decomposed with dilute ammonia, the dry product melted not sharply at 133°. However, on crystallizing this once from considerable low-boiling ligroïn, it came down in the form of lozenges and flattened bunches of crystals, representing exactly methenyldiparatolyl-

* In describing methenyldiparatolylamidine as new, Walther overlooks the fact that this amidine was obtained by Senier (Ber. d. chem. Ges., xviii, 2294). Later this amidine and also methenyldimetanitrophenylamidine (dinitrodiphenylformamidine) was described in Amer. Chem. Jour., xviii, 517, by Comstock and others.

amidine when crystallized under the same conditions. In this form when dry it melted fairly well at 140°.

The above results show that the material obtained by this method, and melting at about 132°, is a mixture which, when crystallized, gives methenyldiparatolylamidine.

The Products Obtained by the Third and Fourth Methods.

The third method consists in treating *p*-formtoluide with aniline and phosphorus trichloride. No details are given for the conversion of the reaction-product into the amidine. It is stated that from petroleum ether the amidine separates in needles melting at 98°.

An experiment according to this method, using the quantities given by Walther, was performed as follows: 5 g. *p*-formtoluide and 3.6 g. of aniline were mixed and treated with an excess of phosphorus trichloride.

A violent reaction took place, and the mass solidified. The material was washed with water, taken up in alcohol, and precipitated with dilute ammonia, dried, and crystallized from petroleum ether, as directed. It then separated in needles or prisms according to the conditions already stated in the introduction. The material, after one crystallization from petroleum ether, melted at 102°–103°, and showed no signs of melting at 98°. After four crystallizations from ligroïn the material melted at 103.5°–104°.

In another experiment 10 g. of *p*-formtoluide, melting at 52°, and 7.2 g. of freshly distilled aniline were mixed; then phosphorus trichloride was slowly added in excess. The product thus obtained was treated as in the previous experiment. The free amidine was crystallized sixteen times from petroleum ether. It separated in needles and prisms, and the following are some of the melting-points which were observed:

I.	97.0°– 97.5°	IX.	102.0°–102.5°	XIV.	103.5°–104°
III.	98.0°–100.0°	XI.	102.5°–103.0°	XV.	103.5°–104°
VI.	100.5°–101.5°	XIII.	103.0°–104.0°	XVI.	103.5°–104°

In another experiment a specimen of *p*-formtoluide was used which was carefully freed from all traces of *p*-toluidine, and which after several crystallizations from ether melted sharply from 53°–54°. This gave the same result as stated in the first experiment above.

Several attempts were made to prepare this amidine from specimens of crude *p*-formtoluide melting at 52°, and from which *p*-toluidine had not been removed by treating with dilute hydrochloric acid and water. In these cases products were obtained melting at about 85°, and in one of these cases the material was crystallized seven times from ligroïn without raising its melting-point above 86°. On the other hand, when pure *p*-formtoluide was used, even the crude product melted higher than this. The lowering of the melting-point in these cases is, therefore, due to the presence of *p*-toluidine in the *p*-formtoluide used.

The fact that the amidine prepared by the third method, and from pure materials, melts lower than when prepared by the fourth, is now readily explained as follows: The phosphorus trichloride decomposes a small part of the *p*-formtoluide into *p*-toluidine hydrochloride, and this, by taking part in the reaction, effects a contamination (probably methenyldiparatolylamidine) that is difficult or impossible to remove by repeated crystallizations. On the other hand, the conditions in the fourth method are different. In that case there is no *p*-formtoluide present to form methenyldiparatolylamidine, and, if the formyl compound is decomposed, aniline is separated, this then forms methenyldiphenylamidine, which is more soluble in petroleum ether than the chief product, the mixed amidine. Hence the material prepared by the fourth method is more readily purified.

An experiment, according to the fourth method, gave the following result: 5 g. of formanilide and 4.8 g. of *p*-toluidine were mixed and treated precisely as in the above experiment. The product from petroleum ether came down in needles or prisms, and after four crystallizations melted from 103.5° to 104.5°.

From the above results it is concluded that only one methenylphenylparatolylamidine exists. In conclusion, the author expresses his indebtedness to Mr. J. A. Hall, who has assisted him in the present work.

NEW HAVEN, March, 1897.

ON THE MOLECULAR REARRANGEMENT OF THE OXIMES BY MEANS OF CERTAIN METALLIC SALTS.*

BY WILLIAM J. COMSTOCK.

THE conversion of ordinary benzaldoxime into its stereoisomer was discovered by Beckmann, who effected it first † by the action of sulphuric acid, afterwards ‡ by the action of hydrochloric acid gas on the ethereal solution. This latter method has since been applied with success to other cases.

The Beckmann rearrangement of an oxime into amide or substituted amide is effected by means of phosphorus pentachloride, § strong sulphuric acid, ‖ acetyl chloride, ¶ and the so-called Beckmann mixture.** I have found that several metallic salts are capable of producing the same results. A good example of this is furnished by the behavior of cuprous chloride towards benzantialdoxime. When a cold solution of ordinary benzaldoxime in dry benzene or toluene is treated with cuprous chloride, the chloride dissolves rapidly. If the solution is a concentrated one, the formation of long needles can be noticed at once; if the solution is dilute, the same compound can be precipitated by the addition of petroleum ether. The new compound is an addition-product of two molecules of oxime to one of cuprous chloride, reckoned as CuCl. But instead of being an addition-product of the antioxime, it contains the stereoisomer.

If the benzene or toluene solution is shaken for a few minutes with an excess of cuprous chloride, and the filtered solu-

* Amer. Chem. Jour., xix, No. 6.

† Ber. d. chem. Ges., xx, 2766.

‡ Ibid., xxii, 433.

§ Beckmann, Ibid., xix, 988.

‖ Beckmann, Ibid., xx, 1507.

¶ Victor Meyer and Warrington, Ibid., 500.

** Ibid., 2581.

tion heated, a separation of cuprous chloride begins at once. After continued boiling and concentrating the filtered solution, benzamide separates. I have tested the behavior of several oximes, and found in each case that addition-products with cuprous chloride or cuprous bromide could be obtained. This is true of both aldoximes and ketoximes and in each case the composition of the product was

$$(\text{Oxime})_2 + \text{CuCl or CuBr}.$$

The rearrangement into amide or substituted amide by boiling a solution of the cuprous-halide-oxime, is not, however, a general reaction, and where effected is not necessarily a smooth one. When the solution of cuprous-halide-oxime is heated, there is usually, if not always, to some extent a regeneration of aldehyde or ketone. In some cases the greater part of the oxime is decomposed in this latter way. For instance, on boiling a toluene solution of benzophenoneoxime with cuprous bromide, the greater part was found to be converted into benzophenone.

The tendency of an oxime to form a "molecular compound" with cuprous chloride is so great that in two cases, at least, *cupric* chloride is reduced to *cuprous* chloride. Benzaldoxime and acetoxime are the two compounds whose behavior towards cupric chloride has been studied.

If an aqueous solution of cupric chloride is added to a concentrated aqueous solution of acetoxime, the separation of colorless crystals begins at once, even at low temperature. With very dilute solutions the separation is slower, but the same reaction takes place. These crystals are identical in composition with those formed by the direct action of cuprous chloride on acetoxime dissolved in an anhydrous solvent. As soon as the separation of crystals from the aqueous solution of oxime and cupric chloride begins, the solution shows the presence of nitrous acid by its reaction with potassium iodide solution.

Obviously a portion of the oxime is split into acetone and hydroxylamine, which latter reduces the cupric chloride to

cuprous chloride with formation of nitrous acid, while another portion of oxime unites with the cuprous chloride to form the difficultly soluble cuprous-chloride-oxime.

In addition to cuprous chloride and cuprous bromide, antimony trichloride effects the Beckmann rearrangement with the greatest ease. This I have shown in the case of benzophenoneoxime.

As a method of converting an antialdoxime into its stereoisomer, the action of hydrochloric acid on the ethereal solution is obviously simpler than the action of cuprous chloride or cuprous bromide. Nevertheless these changes of the oximes under the influence of metallic salts are not without interest. Whether the action of a metallic salt can lead to the discovery of a missing stereoisomeric oxime when other methods fail, is of course uncertain. No special efforts have been made with this in view, as the group has already been worked up with considerable thoroughness.

In compounds other than oximes, but containing the group —N=C—, the methods of obtaining the two stereoisomeric forms are by no means as satisfactory; and there is no *a priori* reason why, in some of these other cases, a rearrangement should not be effected by the action of metallic salts.

Cuprous chloride, cuprous bromide, and antimony trichloride, all add, with the greatest ease, to some of Schiff's bases. A few of these derivatives I shall describe in another paper.

Experimental Part.

Cuprous-chloride-benzsynaldoxime, $(C_6H_5CH{=}NOH)_2CuCl$. —The best method of preparing this compound is by treating a cold solution of ordinary benzaldoxime in dry toluene with a slight excess of cuprous chloride, shaking gently until no more chloride dissolves. From the filtered solution the cuprous-chloride-oxime can be precipitated by the addition of petroleum ether. The toluene solution can even be warmed gently. On working with weighed quantities it was found that the solution of ordinary benzaldoxime dissolved a little less cuprous chloride than is represented by the above com-

position. The compound crystallizes in needles which are at first practically colorless, although the solution assumes at once a yellowish-brown color. The crystals become dark on standing in contact with the mother-liquor, and become dark-green very quickly when exposed to the air.

The compound has no sharp melting-point. Washed with petroleum ether and dried *in vacuo*, it was found to contain 19.1 per cent of copper. The above composition requires 18.59 per cent of copper.

By treatment with cold dilute sodium hydroxide solution the copper can be removed, and on leading carbonic acid into the filtered solution, benzsynaldoxime separates at once in crystals.

From cupric chloride the compound was obtained as follows: The ordinary oxime was dissolved in alcohol and mixed with an alcoholic solution of cupric chloride; water was then added until the solution became turbid, a drop of hydrochloric acid added, and the mixture kept at ordinary room temperature. The formation of long colorless needles began within a few minutes, but the separation was not complete for several hours. The compound prepared in this way seemed comparatively stable when in contact with the mother-liquor, but showed the same rapid coloration when exposed to the air.

When washed quickly with a small quantity of 50 per cent alcohol, and dried *in vacuo*, it gave the following analytical results:

	Found.	Calculated.
Cu	18.8	18.59
Cl	11.7	10.40

Benzsynaldoxime was obtained from this product in the manner described above. The same compound can be obtained by adding ordinary benzaldoxime to a cold solution of cuprous chloride in dilute hydrochloric acid. When the oxime is added to a cold concentrated solution of cuprous chloride in strong hydrochloric acid, a compound crystallizing in small yellow needles is formed. This yellow compound

is quite unstable, but it contains the oxime as synoxime (shown as above), and is obviously a double salt, as it is formed only in the presence of strong acid. On adding water gradually to this double salt, the formation of the white needles of cuprous-chloride-oxime can be observed.

As to the rearrangement into benzamide, it was carried out in benzene and in toluene solution. The amide was obtained with sharp melting-point after one recrystallization, and was further identified by the formation of ammonia and benzoic acid. The cuprous chloride which separated when this rearrangement was effected, was dirty and mixed with some resinous matter after the solution had been heated for a time, although when the separation first began it was light colored, much lighter than the solution. Benzaldehyde and probably benzonitrile are by-products of the reaction.

I have assumed that the copper separates as cuprous chloride or cuprous bromide in this and similar cases, but have not proved this by analysis.

Cuprous bromide acts like the chloride, but I have not analyzed the intermediate product, which, however, seemed more stable than the cuprous chloride compound.

Other Aldoximes. — Cinnamaldoxime gives with cuprous bromide an addition-product crystallizing from toluene in small yellow needles. For this purpose a mixture of the two stereoisomers * was used.

Found.	Calculated for $(Oxime)_2CuBr$.
Cu = 14.52	Cu = 14.49

It was shown that the Beckmann rearrangement is effected by boiling the toluene solution. The amide of cinnamic acid was not purified, but decomposed by boiling sodium hydroxide solution. Pure cinnamic acid was obtained and identified. Much aldehyde was also formed.

Oenanthaldoxime forms a beautifully crystallized product with cuprous bromide when warmed in ligroïn solution. On cooling the filtered solution the product separates in star-like

* See Bamberger and Goldschmidt, Ber. d. chem. Ges., xxvii, 3428.

clusters of long transparent prisms. It proved comparatively stable when exposed to the air; after several hours there was practically no change. The amount of oenanthol regenerated when the toluene solution was boiled seemed large.

Cuprous-chloride-acetoxime, $(C_3H_6NOH)_2CuCl$. — This compound can be prepared in dry benzene, toluene, or ligroïn by the direct action of cuprous chloride. It can be recrystallized advantageously from boiling ligroïn, but undergoes some decomposition on protracted boiling, and changes very quickly on exposure to the air. It crystallizes in colorless transparent plates or inclined prisms, which assume a yellowish color on exposure to the air for a few minutes. The melting-point is not sharp; it softens below 80°, is completely melted at 96°, to a clear fluid of yellowish brown color. On further heating it undergoes energetic decomposition, and has an odor like impure acetamide. The change is, however, essentially a dissociation.

An analysis of the compound crystallized from hot ligroïn gave the following results:

	Found.	Calculated.
Cu	26.17	25.88
Cl	14.61	14.49

The preparation from cupric chloride in aqueous solution has been described in the introduction. An analysis of the compound prepared in this way and dried *in vacuo* without recrystallization gave the following results:

	Found.	Calculated.
Cu	26.70	25.88
Cl	14.83	14.49

On recrystallization from ligroïn the crystals were to the eye exactly like those prepared directly from cuprous chloride.

Cuprous-bromide-acetoxime, $(C_3H_6NOH)_2CuBr$. — Preparation as in the case of the previous compound. The bromide is changed less rapidly on exposure to the air and is more difficultly soluble. It melts to a clear fluid at 121°–122°,

after softening a few degrees below. It occurs as hexagonal plates or thick, transparent, inclined prisms. A copper estimation gave 22.05 per cent, while the theory requires 21.90 per cent.

The Beckmann rearrangement into methylacetamide could not be effected by boiling the toluene solution of either of these acetoxime derivatives. A solution of the cuprous-bromide-oxime was boiled for hours. The solution became dark-colored, and a small quantity of insoluble matter was formed. After boiling off most of the toluene, the entire residue was boiled with strong sodium hydroxide solution, the volatile part being caught in dilute hydrochloric acid. The hydrochloric acid solution left a residue on evaporation, but this residue was not methylamine hydrochloride, as it was not deliquescent and did not give the isonitrile reaction. The distillate from the sodium hydroxide had a distinct bone-oil odor, and this same odor was noticed on adding an alkali to the residue from the hydrochloric acid solution. This suggests the formation of a pyridine base, but I did not obtain sufficient for identification.

Other Ketoximes. — Acetophenoneoxime in toluene solution unites with cuprous chloride. The compound was precipitated by ligroïn in thin colorless plates, which darken quickly. Unchanged oxime was recovered after treating with sodium hydroxide solution, filtering and adding carbon dioxide.

Found.	Calculated.
Cu = 17.7	Cu = 17.2.

Boiling in toluene solution led to dark-colored products not carefully examined. Certainly the reaction is not a smooth one.

Benzophenoneoxime and Cuprous Chloride,

$$\left(\begin{matrix}C_6H_5\\C_6H_5\end{matrix}>C{=}NOH\right)_2 CuCl. —$$

This compound was prepared as follows: The oxime was dissolved in methyl alcohol, an excess of cuprous chloride and a few drops of hydrochloric acid added, the solution warmed

on the water-bath to 60° for a few minutes, and filtered from the excess of chloride. On cooling small, thick, yellow plates were deposited. Unchanged oxime could be recovered.

	Found.	Calculated.
Cu . .	14.08	12.86

The compound can be obtained in large diamond-shaped, doubly-terminated plates of yellow color, when an excess of cuprous chloride is dissolved, together with the oxime in a mixture of hydrochloric acid, methyl alcohol, and chloroform, and the solution evaporated quickly at ordinary temperature. A toluene solution of the oxime boiled in presence of cuprous chloride, or cuprous bromide, yielded essentially benzophenone.

Rearrangement with Antimony Trichloride.—When benzophenoneoxime is added in small portions to the antimony trichloride warmed just above its melting-point, the oxime dissolves to a clear solution with but a trace of color. The addition of each portion of oxime produces a hissing sound, and if a large quantity of oxime is added at once, the reaction becomes violent and the product dark-colored.

On slowly adding 1.8 g. of oxime to 6 g. of trichloride, washing the product with a mixture of alcohol and dilute hydrochloric acid, and recrystallizing the residue from alcohol, a yield of 1.5 g. of pure benzanilide is obtained.

SHEFFIELD CHEMICAL LABORATORY,
March, 1897.

ON HALOGEN ADDITION-PRODUCTS OF THE ANILIDES.*

[THIRD PAPER.]

By H. L. WHEELER, BAYARD BARNES, AND J. H. PRATT.

In a recent paper from this laboratory † it was shown that the anilides are capable of forming addition-products with bromine and iodine, and that these addition-products can only be formed in the presence of a halogen acid. They are, therefore, perhalides, and it was concluded that these compounds are derivatives of substituted ammonium salts, and that they are perfectly analogous to the perhalides of cæsium ‡ and ammonium.§

We have continued the study of these compounds in order to test the correctness of this view, and also with the object of determining the structure of the halogen salts of the anilides. We have made crystallographic measurements of some of the perhalides and of ammonium triiodide, and we find that, although ammonium triiodide is perfectly analogous to the perhalides of the alkali metals, on the other hand, the perhalides of the anilides, as far as examined, show no crystallographic analogy whatever with these compounds.

This, perhaps somewhat unexpected, result would indicate that the peculiar salts from which the perhalides are derived are not substituted ammonium compounds, and it will be seen below that other experimental work confirms this conclusion.

* Amer. Chem. Jour., xix, No. 8.
† Wheeler and Walden, Ibid., xviii, 85.
‡ Wells, Amer. Jour. Sci., xliii, 17.
§ Roozeboom, Ber. d. chem. Ges., xiv, 2398.

All these perhalides are derivatives of two molecules of an anilide with one of a halogen acid, or, briefly, of the 2 : 1 salts. Perhalides derived from 1 : 1 salts have not been prepared. When these salts are employed, the products obtained are invariably derivatives of 2 : 1 salts. However, no special attempt has been made to decide whether the 1 : 1 salts are capable of forming perhalides.

Nölting and Weingärtner * were the first to prepare a 2 : 1 salt of the anilides. They found that acetanilide and hydrogen chloride gave a compound represented by the formula $(C_6H_5NHCOCH_3)_2HCl$, and they investigated its behavior on heating. At 250° they obtained ethenyldiphenylamidine, at 280° flavaniline, and at 300° dimethylquinoline. The 1 : 1 hydrochloride of acetanilide was observed by Knorr. †

Our work with these salts has shown that the anilides in general form these two series of salts, and no other types have been observed. The anilides differ from their pseudo derivatives, *i. e.*, the imido-esters, both in forming 2 : 1 salts, as well as in not forming 1 : 2 salts. These salts are characteristic for the two series. It is now interesting to note that formanilide gives 2 : 1 salts in the same manner in which the corresponding salts of the other anilides are obtained. The conclusion that follows from this is that formanilide belongs to the series of anilides, and that it has the normal structure.

At present there is no occasion to assume that the 1 : 1 salts are anything but substituted ammonium compounds. In the case of the 2 : 1 salts, it is different, and here numerous constitutional formulas are theoretically possible. It will be convenient to discuss these under three heads:

I. Those which are represented as having the pseudo form of the anilide.

II. Those in which oxygen or the acyl group takes part in the union of the molecules.

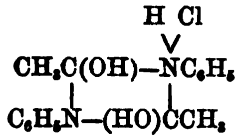
III. The diammonium structure.

The following formulas are examples of these types:

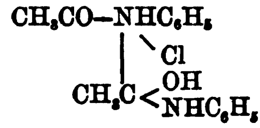
* Ber. d. chem. Ges., xviii, 1340.

† Ann. Chem. (Liebig), ccxlv, 375.

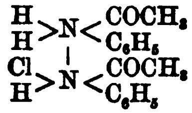
I.



II.



III.



The first type is excluded, since we find that methylmetanitroacetanilide gives perhalides of a 2 : 1 salt, and also since this is an ammonium salt.

In regard to the second type, it may be stated that the presence of oxygen, *i. e.*, an acyl group, is unnecessary for the formation of 2 : 1 salts, or of their perhalides. Troost * has prepared the compounds $2NH_3.HBr$ and $2NH_3.HI$, and Grimaux † has described a perhalide of pyridine represented by the following formula: $(C_5H_5N)_2HBr.Br_4$. Another compound that evidently belongs to this class is the iodine addition-product of benzamide obtained by Curtius: ‡

$$\begin{array}{c} C_6H_5CONH_2.I \\ | \\ C_6H_5CONH_2.I \end{array}$$

On account of these facts, and since the 2 : 1 salts of the anilides are not derived from the pseudo form, the diammonium structure III seems to be most satisfactory. This structure readily allows for the formation of 2 : 1 salts from the secondary anilides, and also explains the lack of analogy of the perhalides to those of ammonium.

A comparison of the perhalides of the anilides with those of the alkali metals shows other interesting differences besides the lack of analogy in crystalline form.

In this paper we describe mixed perhalides, and show that the hydrochloric acid salts of the anilides readily give per-

* Compt. rend., xcii, 715. † Bull. Soc. Chim. (Paris), xxxviii, 127.
‡ Ber. d. chem. Ges., xxiii, 3040.

halides with iodine, while the corresponding perhalides of the alkali metals could not be obtained.

In the case of the bromides and iodine only $CsBrI_2$* could be obtained, rubidium and potassium having little or no tendency to form this perhalide. On the other hand, the hydrobromides of the anilides readily unite with iodine, methylmetanitroacetanilide hydrobromide giving a tetra addition-product.

The relative stability of these perhalides is similar to those of the alkali metals, those containing only iodine being the most stable. Large crystals of the compound $(C_6H_5NHCOCA_3)_2HI.I_2$, after standing in a corked tube for over a year, gave excellent reflections on the goniometer.

The property of forming perhalides, and the relatively greater stability of these perhalides, when compared to some of the alkaline metal derivatives, show that it is not basicity that determines their stability or tendency to form, since the salts of the anilides are decomposed by water.

Experimental Part.

Ammonium Triiodide, $NH_4I.I_2$. — This salt was prepared by dissolving the calculated amount of iodine in a strong solution of ammonium iodide and evaporating by standing over potash, as described by Johnson,† when dark blue prisms were obtained. These belong to the orthorhombic system, and the faces which were observed are as follows:

a, 100	*c*, 001	*d*, 011	*i*, 103
b, 010	*m*, 110	*e*, 102	

The axial ratio derived from the angles marked with an asterisk in the table below is:

$$a : b : c = 0.6950 : 1 : 1.1415$$

The crystals are somewhat peculiar in their development, for they show two very similar forms which have no faces alike. They attained a length of 3 mm.

* Wells, loc. cit.

† Ber. d. chem. Ges., ii, 1268.

Fig. 1 represents the first form, where the prism *m*, 110 and the dome *i*, 103 are about equally developed, giving the crystals nearly a square outline. The second form of crystals,

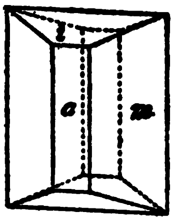


Fig. 1.

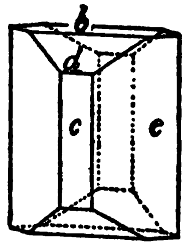


Fig. 2.

Fig. 2, has nearly the same outline, due to the nearly equal development of the domes *d*, 011 and *e*, 102. The base *c*, 001 has been drawn in front in order to show, to better advantage, the similarity between the two forms. The crystals were generally well developed, but the faces were apt to be dull and somewhat rounded, so that in some cases only approximate measurements could be obtained.

The similarity in the crystallization of ammonium triiodide and the alkali metal trihalides, described by Wells, Wheeler, and Penfield,* is very striking, and in the following table the corresponding angles of the alkali triiodides are given for comparison:

		Measured.	Calculated.			
		NH_4I_3.	NH_4I_3.	KI_3.	RbI_3.	CsI_3.
$110 \wedge \bar{1}10$,	$m \wedge m'''$	*69° 36′	. . .	70° 34′	68° 53′	68° 37′
$102 \wedge \bar{1}02$,	$e \wedge e'$	*78° 50′	. . .	. . .	78° 38′	78°
$100 \wedge 011$,	$c \wedge d$	48° 26′–48° 45′	48° 47′	. . .	48° 19′	47° 51′
$102 \wedge 011$,	$e \wedge d$	60° 3′	59° 24′	. . .	. . .	. . .
$103 \wedge \bar{1}03$,	$i \wedge i'$	57° 15′	57° 30′	. . .	. . .	. . .
c, axis,	. . .	. . .	1.1415	. . .	1.1234	1.1051
a, axis,	. . .	. . .	0.6950	0.7065	0.6858	0.6824

From the above the ammonium triiodide is shown to be isomorphous with the alkali metal trihalides, while the trihalides of the anilides, as far as examined, show no similarity

* Amer. Jour. Sci. [III], xliii, 17 and 478.

whatever with the above, the latter crystallizing in either the monoclinic or the triclinic system.

Experiments with Acetanilide.

The 2 : 1 and 1 : 1 *hydrochlorides* of acetanilide † separate from an ethyl-acetate or a chloroform solution as a granular precipitate, generally in the form of a mixture, when the solutions are treated with dry hydrogen chloride. The simple salts of the anilides were not obtained in crystals suitable for measurement.

The Iodhydrochloride, $(C_6H_5NHCOCH_3)_2HCl.I_2$.—This salt, as well as the other perhalides described in this paper, was prepared by dissolving the constituents (either the 2 : 1 or 1 : 1 salts and the halogen) in hot glacial acetic acid, and then cooling. The crystals for measurement were generally obtained by slowly evaporating the solution in glacial acetic acid over potassium hydroxide in a desiccator. Better crystals were obtained in this manner than by slowly cooling in a felt box. The crystals in each case were washed free from acetic acid by means of chloroform, and after drying by pressing on paper, were analyzed. The analytical results have been obtained in the gravimetric way; determination of mixed halogens have been made by igniting the silver salts in a current of chlorine in the usual manner.

Acetanilide iodhydrochloride, prepared as above, separated in the form of dark-blue, shining needles; crystals suitable for measurement were not obtained. This and the corresponding salt of parabromacetanilide are the least stable of the perhalides; they soon lose iodine and turn white.

	Calculated for $C_{16}H_{18}N_2O_2.HCl.I_2$.	Found.
I	45.3	45.9
Cl	6.3	6.6

The 1 : 1 Hydrobromide, $C_6H_5NHCOCH_3.HBr$.—This was obtained as a colorless crystalline precipitate. It apparently contained a slight admixture of the 2 : 1 salt.

* Loc. cit.

	Calculated for $C_8H_9NO.HBr$.	Found.
Br	37.0	35.1

The Iodhydrobromide, $(C_6H_5NHCOCH_3)_2HBr.I_2$, prepared from the above salt, separated in dark-red prisms.

	Calculated for $C_{16}H_{19}N_2O_2.HBr.I_2$.	Found.
I	41.9	41.2
Br	13.2	13.4

The crystallization of acetanilide iodhydrobromide is triclinic, and the following faces have been observed:

c, 001	*m*, 110	*p*, $\bar{1}\bar{1}1$
b, 010	*M*, $1\bar{1}0$	*x*, $\bar{4}03$

The axial ratio derived from the angles marked by the asterisk in the table below was found to be:

$$a : b : c = 0.5707 : 1 : 1.2005;\ \alpha = 89^\circ\ 26',$$
$$\beta = 132^\circ\ 20',\ \gamma = 83^\circ\ 16'.$$

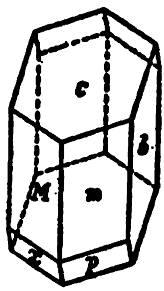


Fig. 3.

The crystals were small, not over 1.5 mm. in length, and were generally doubly terminated. Fig. 3 represents the form of the crystals.

The faces were smooth, and gave fair reflections of the signal on the reflecting goniometer. In the table of angles the two extremes of three or more measurements are given.

		Measured.	Calculated.
$c \wedge m$,	$001 \wedge 110$	*52° 6′	. . .
$c \wedge b$,	$001 \wedge 010$	*83° 2′	. . .
$c \wedge p$,	$001 \wedge \bar{1}\bar{1}1$	*66° 3′	. . .
$c \wedge M$,	$001 \wedge 1\bar{1}0$	50° 36′–50° 58′	50° 47′
$m \wedge b$,	$110 \wedge 010$	74° 50′–74° 55′	74° 55′
$m' \wedge p$,	$\bar{1}\bar{1}0 \wedge \bar{1}\bar{1}1$	61° 48′–61° 49′	61° 51′
$b \wedge m$,	$0\bar{1}0 \wedge 1\bar{1}0$	*58° 11′	. . .
$m \wedge M$,	$110 \wedge 1\bar{1}0$	*46° 54′	. . .

The 2 : 1 Hydroiodide, $(C_6H_5NHCOCH_3)_2HI$. — This, and not the 1 : 1 salt, was obtained, both from chloroform and

ethyl-acetate solutions of the anilide, on saturating with hydrogen iodide. It is a noticeable fact that hydrogen iodide forms 2 : 1 salts more readily than the other halogen acids.

The Iodhydroiodide, $(C_6H_5NHCOCH_3)_2HI.I_2$. — This and the above hydroiodide were described in a previous paper. This perhalide has the greatest tendency to crystallize, some of the crystals being 3 mm. in diameter and 10 mm. in length. They crystallize in the triclinic system, and only three faces were observed which could be determined. These have been taken as the three pinacoids, *c*, 001; *b*, 010; and *a*, 100. On a few crystals other faces were observed, but they could not be identified.

The inclinations of the axes calculated from the angles of pinacoids, are as follows:

$$\alpha = 102^\circ\ 56'; \ \beta = 104^\circ\ 34'; \ \gamma = 113^\circ\ 2'.$$

$a \wedge b$, 100 $\wedge$ 010	61° 40′
$a \wedge c$, 100 $\wedge$ 001	67° 47′
$b \wedge c$, 010 $\wedge$ 001	68° 47′

Experiments with Parabromacetanilide.

The 2 : 1 Hydrochloride, $(C_6H_4.Br.NHCOCH_3)_2HCl$. — The formation of 1 : 1 salts in the case of parabromacetanilide was not observed. This compound was obtained as a colorless, crystalline precipitate.

	Calculated for $C_{16}H_{16}N_2O_2Br_2.HCl$.	Found.
Cl	7.6	6.6

The Iodhydrochloride, $(C_6H_4Br.NHCOCH_3)_2.HCl.I_2$ was obtained as dark-violet needles.

	Calculated for $C_{16}H_{16}N_2O_2Br_2.HCl.I_2$.	Found.
I	35.3	35.3
Cl	4.9	5.2

The 2 : 1 Hydrobromide, $(C_6H_4BrNHCOCH_3)_2HBr$, previously described, gave:

The Iodhydrobromide, $(C_6H_4BrNHCOCH_3)_2HBr.I_2$, in the form of red prisms.

	Calculated for $C_{16}H_{16}N_2O_2Br_2HBr.I_2$.	Found.
I	33.2	31.1
Br	10.5	10.6

The 2 : 1 Hydroiodide, $(C_6H_4BrNHCOCH_3)_2HI$, was obtained as a colorless, crystalline precipitate.

	Calculated for $C_{16}H_{16}N_2O_2Br_2.HI$.	Found.
I	22.8	22.3

The Iodhydroiodide, $(C_6H_4BrNHCOCH_3)_2HI.I_2$, prepared from the above, separated in dark-red, triclinic crystals. These attained a diameter of 0.5 mm. The faces observed are the following:

a, 100; m, 110; x, $\bar{1}01$; n, 011.

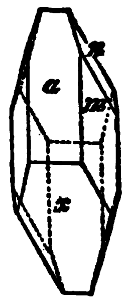


Fig. 4.

The faces were smooth and bright and gave good reflections. From the angles marked by an asterisk in the table below, the following axial ratio was determined:

$$a : b : c = 1.853 : 1 : 3.015;\ \beta = 79°\ \tfrac{1}{2}'.$$

		Measured.	Calculated.
$a \wedge n$,	$\bar{1}00 \wedge 011$	*93° 30′	. . .
$m \wedge n'$,	$110 \wedge 0\bar{1}1$	*142° 40′	. . .
$a \wedge m$,	$\bar{1}00 \wedge 110$	*61° 31′	. . .
$a' \wedge x$,	$\bar{1}00 \wedge \bar{1}01$	34° 28′	34° 24′
$m''' \wedge d'$,	$\bar{1}10 \wedge 0\bar{1}1$	30° 28′	30° 43′
$d \wedge x$,	$011 \wedge \bar{1}01$	82° 47′	82° 45½′
$m' \wedge x$,	$\bar{1}10 \wedge \bar{1}01$	66° 35′	66° 35½′
$m'' \wedge d'$,	$\bar{1}\bar{1}0 \wedge 0\bar{1}1$	36° 44′	36° 46′

The Iodhydroiodide, $(C_6H_4BrNHCOCH_3)_2HI.I_4$, was obtained in the form of deep-red, monoclinic twins. Enough faces were not shown to permit of satisfactory crystallographic description.

	Calculated for $C_{16}H_{16}N_2O_2Br_2HI.I_4$.	Found.
I	59.68	59.75

Experiments with Methylmetanitroacetanilide.

The 1 : 1 Hydrobromide, $C_6H_4NO_2NCH_3COCH_3.HBr$. — This and not the 2 : 1 salt was obtained directly in the form of a colorless, crystalline precipitate.

	Calculated for $C_9H_{10}N_2O_3.HBr$.	Found.
Br	29.0	28.3

The Bromhydrobromide, $(C_6H_4NO_2NCH_3COCH_3)_2HBr.Br_2$. — The above 1 : 1 salt gave this perhalide in the form of small dark-yellow, well-developed, stout prisms. It slowly evolves bromine on exposure.

	Calculated for $C_{18}H_{20}N_4O_6HBr.Br_2$.	Found. I.	II.
Br	38.1	37.2	37.4

The Iodhydrobromide, $(C_6H_4NO_2NCH_3COCH_3)_2HBr.I_4$. — This was obtained as a black mass, which under the microscope appeared to consist of needles. The powder was dark bottle-green.

	Calculated for $C_{18}H_{20}N_4O_6HBr.I_4$.	Found.
Br	8.1	8.1
I.	51.9	52.8

When hydrogen iodide was passed into an ethyl acetate solution of methylmetanitroacetanilide, the acid was reduced and no precipitate was formed.

Experiments with Formanilide.

The 2 : 1 Hydrochloride, $(C_6H_5NHCHO)_2HCl$. — When hydrochloric acid is passed into a solution of formanilide in dry benzene, the product obtained is generally a mixture of the 2 : 1 and 1 : 1 salts. The 2 : 1 salt was obtained as a colorless, crystalline precipitate, which soon absorbed moisture and decomposed on exposure.

	Calculated for $C_{14}H_{14}N_2O_2.HCl$.	Found.
Cl	12.7	12.3

The 2 : 1 Hydroiodide, $(C_6H_5NHCHO)_2HI$. — The salt, obtained apparently in the form of needles from a benzene solu-

tion, rapidly absorbs moisture from the air, becoming sticky and decomposing. For analysis it was rapidly pressed on paper and dried over sulphuric acid in a vacuum-desiccator. The analysis indicates that a slight decomposition was not avoided:

	Calculated for $C_{14}H_{14}N_2O_2HI$.	Found.
I	34.3	31.2

The 1 : 1 Hydroiodide, $C_6H_5NHCHO.HI$, differs decidedly in appearance from the above 2 : 1 salt. It separates from an ethyl-acetate solution in granular condition, and is more stable. An iodine determination gave 48.0 per cent of the halogen instead of the 51.0 per cent.

Attempts were made to prepare perhalides from the salts of formanilide, but when these were warmed in glacial acetic acid the anilide was saponified. Similar results were obtained with the salts of paraformtoluide, the salts of the formyl compounds being considerably less stable than those containing the acetyl group.

Other Experiments.

The 2 : 1 Hydrochloride, $(C_6H_4NO_2NHCOCH_3)_2HCl$, was obtained from a chloroform-solution of metanitroacetanilide and hydrogen chloride.

	Calculated for $C_{16}H_{16}N_4O_6.HCl$.	Found.
Cl	8.9	8.7

Under similar conditions methylacetanilide, dipenylbenzamide, diethylbenzamide, and methylbenzanilide gave no precipitate with either hydrogen chloride or bromide, ethyl acetate or chloroform being used as the solvent. Benzamide was not precipitated from a chloroform solution by hydrogen chloride, although this amide gives salts with the halogen acids. From ethyl acetate hydrogen chloride and bromide precipitated the 1 : 1 salts of paraformtoluide, and from benzene, benzamide was precipitated as a 1 : 1 salt by hydrogen iodide.

NEW HAVEN, May, 1897.

ON DIACYL ANILIDES.*

By H. L. WHEELER, T. E. SMITH, AND C. H. WARREN.

It has frequently been observed that formanilide shows a departure from the other anilides in many of its properties, and it has been stated that this would seem to indicate that it is not an anilide or, in other words, that it does not contain the formyl group $—C\genfrac{}{}{0pt}{}{\diagup H}{\diagdown\!\!\diagdown O}$.

In the diacyl anilides the formyl group exists as represented above, and it seemed of interest to compare crystallographically the formyl derivative in one of these series with those of its homologues. We have, therefore, prepared the following series of diacyl anilides, and find that some of these compounds are especially suitable for a crystallographic examination:

Formylbenzenesulphanilide, $C_6H_5N<\genfrac{}{}{0pt}{}{CHO}{SO_2C_6H_5}$.

Acetylbenzenesulphanilide, $C_6H_5N<\genfrac{}{}{0pt}{}{COCH_3}{SO_2C_6H_5}$.

Propionylbenzenesulphanilide, $C_6H_5N<\genfrac{}{}{0pt}{}{COCH_2CH_3}{SO_2C_6H_5}$.

n-Butyrylbenzenesulphanilide, $C_6H_5N<\genfrac{}{}{0pt}{}{COCH_2CH_2CH_3}{SO_2C_6H_5}$.

Benzoylbenzenesulphanilide, $C_6H_5N<\genfrac{}{}{0pt}{}{COC_6H_5}{SO_2C_6H_5}$.

Benzoylbenzenesulph-α-naphthalide,
Benzoylbenzenesulph-β-naphthalide, $C_{10}H_7N<\genfrac{}{}{0pt}{}{COC_6H_5}{SO_2C_6H_5}$.

The results of the crystallographic examination of these compounds show that acetyl and propionylbenzenesulphanilide exhibit close crystallographic analogy, the compounds being monoclinic, hemimorphic, and pyroelectric, their crystallographic axes and the angle β being similar.

* Amer. Chem. Jour., xix, No. 9.

On the other hand, formylbenzenesulphanilide, which is orthorhombic, shows no analogy whatever with these compounds. It may be added that crystals of formanilide which we obtained show no analogy with those of acetanilide.

Since a compound with the true formyl group may exhibit a departure in physical properties from those of the homologues it follows that a similar departure in physical properties in the case of formanilide, formic acid,* etc., cannot be taken as evidence against the presence of the group $-C\begin{matrix} \diagup H \\ \diagdown\!\!\diagdown O \end{matrix}$ in these compounds.

Knight † has recently investigated the action of benzoyl chloride on benzenesulphanilide on the one hand, and of benzenesulphochloride on benzanilide on the other, with the expectation of obtaining benzoylbenzenesulphanilide if benzanilide has the normal structure. As a matter of fact, the reactions did not proceed as expected, but in both cases dibenzanilide was formed.

Believing this result to be due to the secondary action of hydrogen chloride, which is formed in both reactions, we have heated benzoylbenzenesulphanilide with dry hydrogen chloride, and have found that benzoyl chloride was liberated, and also that the diacyl anilide, in the presence of benzoyl chloride, is readily converted into dibenzanilide.

The explanation of the formation of dibenzanilide in the case of Knight's experiment is therefore as follows: Benzoylbenzenesulphanilide is first formed in both cases, and a portion of this in the presence of the resulting hydrogen chloride forms benzoyl chloride, which converts the remaining benzoylbenzenesulphanilide into dibenzanilide. This is the more probable, since Knight states that in both cases the same phenomena were observed. Moreover, it has been customary to prepare diacylsulphamides by heating the sulphamides with acyl chlorides. These results are, therefore, in favor of the normal structure for benzanilide.

* Freer and Sherman, Amer. Chem. Jour., xviii, 526.
† Ibid, xix, 152.

The diacyl anilides containing the benzenesulpho groups behave with alkali precisely like the other mixed diacyl anilides. In each case, so far as examined, the lower acyl group is first removed.*

The authors take pleasure in acknowledging their great indebtedness to Professor S. L. Penfield, under whose direction the following crystallographic results were obtained:

Experimental Part.

Formylbenzenesulphanilide, $C_6H_5N{<}{CHO \atop SO_2C_6H_5}$. — This compound was prepared by acting on phenylformimidoethyl ester with benzenesulphochloride, as previously described.† The structure assigned to this substance follows from its method of preparation and its subsequent decomposition with alkali. The crystals for measurement were obtained from absolute alcohol in each case. Formylbenzenesulphanilide is orthorhombic, and the following forms were observed:

a, 100	*m*, 110	*e*, 201
b, 010	*d*, 101	*p*, 111

The measurements are as follows, those marked with an asterisk being taken as fundamentals.

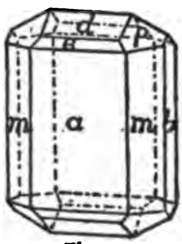


Fig. 1.

		Measured.	Calculated.
$a \wedge e$,	$100 \wedge 201 =$	*55° 53′	. . .
$a \wedge d$,	$100 \wedge 101 =$	71° 15′	71° 17′
$m \wedge m$,	$110 \wedge 1\bar{1}0 =$	*67° 44′	. . .
$d \wedge d$,	$101 \wedge \bar{1}01 =$	37° 25′	37° 25′
$p \wedge d$,	$111 \wedge 101 =$	23° 17′	23° 18′
$p \wedge a$,	$111 \wedge 100 =$	72° 51′	72° 50′
$p \wedge p$,	$111 \wedge \bar{1}11 =$	34° 14′	34° 18′
$b \wedge p$,	$010 \wedge 111 =$	66° 39′	66° 42′

axes $a : b : c = 0.6711 : 1 : 1.0993$.

The crystals of formylbenzenesulphanilide present the habit shown in Fig. 1. They were small when compared with

* Compare also Remsen and Palmer, Amer. Chem. Jour., viii, 243.
† Wheeler and Walden, Ibid., xix, 135.

some of the other diacyl anilides, rarely exceeding 5 mm. in length. They have a tendency to grow in the direction of the *b* axis. On the majority of the crystals it was found that the full number of the *e* and *d* faces were not developed, thus giving the crystals a decidedly monoclinic aspect.

Acetylbenzenesulphanilide, $C_6H_5N{<}{COCH_3 \atop SO_2C_6H_5}$. — This and the following diacyl anilides were prepared by acting on the sodium salts of the sulphanilide in dry benzene with acid anhydrides. Their formation results more smoothly in this manner than when the sulphanilides are heated with acid chlorides. The structure assigned to these substances follows from their method of preparation, since Blacher * has shown that the sodium salt of benzamide gives with benzoic and acetic anhydrides dibenzamide and acetbenzamide, and these diacylamides have both acyl groups attached to nitrogen, as proved conclusively by Wheeler and Walden.†

Acetylbenzenesulphanilide separates from very dilute solutions in the form of large, rough, colorless, monoclinic plates, having a tendency to form clusters. From more concentrated solutions small, finely developed crystals, 1 to 2 mm. in length, grow, while from still more concentrated solutions the substance comes down in long thin needles. When the material was crystallized from alcohol, it melted constantly at 116.5°. A nitrogen determination gave the following result:

	Calculated for $C_{14}H_{13}NO_3S$.	Found.
N	5.09	4.91

The crystals are hemimorphic, as shown in Fig. 2. The forms observed are:

a, 100	*s*, $\bar{1}01$	*p*, $\bar{1}11$
b, 010	*d*, 011	
c, 001	d_1, $0\bar{1}1$	

The faces *b*, *d*, and *p* were observed at that extremity of the *b* axis, where negative electricity developed, when the crystals,

* Ber. d. chem. Ges., xxviii, 2356. † Loc. cit.

which had been heated for some time, were cooled, while at the other extremity *d* alone occurred.

The measurements obtained are as follows:

	Measured.	Calculated.
$a \wedge c$, 100 ∧ 001 =	*64° 56′	. . .
$d \wedge d$, 011 ∧ 01$\bar{1}$ =	*75° 59′	. . .
$c \wedge s$, 001 ∧ $\bar{1}$01 =	*63° 56′	. . .
$c \wedge d$, 001 ∧ 011 =	51° 59′	52° 0½′
$a \wedge d$, 100 ∧ 011 =	75° 0′	74° 52′
$a \wedge p$, $\bar{1}$00 ∧ $\bar{1}$11 =	64° 52′	65° 2′
$p \wedge d$, $\bar{1}$11 ∧ 011 =	40° 8′	40° 6′
$s \wedge p$, $\bar{1}$01 ∧ $\bar{1}$11 =	47° 44′	. . .
$p \wedge d$, 11$\bar{1}$ ∧ 011 =	84° 48′	84° 49′

Axes = $a : b : c = 1.225 : 1 : 1.4138$. $\beta = 100 \wedge 001 \wedge 64° 59′$.

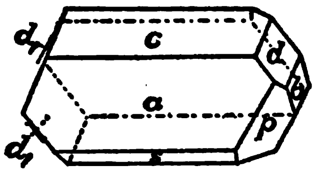


Fig. 2.

Propionylbenzenesulphanilide, $C_6N_5N{<}^{COCH_2CH_3}_{SO_2C_6H_5}$. — The product of the action of propionic anhydrid on sodium benzenesulphanilide was crystallized from absolute alcohol when it melted constantly at 115°.

	Calculated for $C_{15}H_{15}NO_3S$.	Found.
N	4.8	4.7

The crystals are hemimorphic, Fig. 3, representing the prevailing habit, while more complicated crystals, like Fig. 4, were only occasionally found.

The forms observed are:

a, 100	c, 001	d_1, 0$\bar{1}$2
b, 010	n, 3$\bar{1}$0	x, 31$\bar{2}$
b_1, 0$\bar{1}$0	d, 012	x_1, 3$\bar{1}\bar{2}$

The faces x_1 and n_1 are developed at that extremity of the b axis, where positive electricity occurs, when the crystals

which had been heated for some time were cooled. The face x, when observed, was always smaller than x_1, while b and d were about equal in size to b_1 and d_1.

The measurements are as follows:

		Measured.	Calculated.
$a \wedge d$,	$100 \wedge 012 =$	*69° 7′	. . .
$d \wedge d$,	$012 \wedge 0\bar{1}2 =$	*64° 46′	. . .
$a \wedge x$,	$100 \wedge 31\bar{2} =$	*38° 59′	. . .
$a \wedge c$,	$100 \wedge 001 =$	65° 0′	65° 2′
$b \wedge x$,	$010 \wedge 31\bar{2} =$	68° 52′	68° 52′
$a \wedge n_1$,	$100 \wedge 3\bar{1}0 =$	19° 33′	19° 31′
$c \wedge x$,	$00\bar{1} \wedge 31\bar{2} =$	82° 0′	82° 0′
$c \wedge n_1$,	$001 \wedge \bar{3}10 =$	66° 32′	66° 33′
$b \wedge n_1$,	$010 \wedge 3\bar{1}0 =$	70° 27′	70° 29′
$d \wedge x_1$,	$0\bar{1}\bar{2} \wedge 3\bar{1}\bar{2} =$	71° 54′	71° 55′

Axes $= a : b : c = 1.170 : 1 : 1.390$. $\beta = 100 \wedge 001 = 65° 2′$.

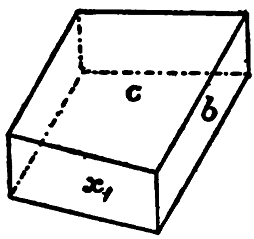


Fig. 3.

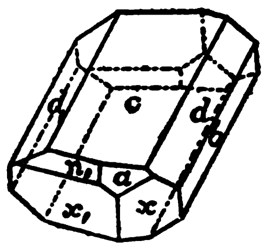


Fig. 4.

From very dilute solutions, containing only a few grams of material, this compound grows in crystals enormously elongated in the direction of the a axis, some of the crystals attaining a length of 75 mm. and a diameter of from 2 to 3 mm. On account of the fact that these crystals show entirely different habits from those of the acetyl compounds, it was thought at first that no analogy in crystalline structure existed between them. By adopting, however, appropriate indices for the faces, a close similarity in the axial ratios of these hemimorphic compounds may be observed as follows:

Acetyl	$a : b : c = 1.225 : 1 : 1.4138$	$\beta = 64° 56′$.
Propionyl	$a : b : c = 1.170 : 1 : 1.390$	$\beta = 65° 2′$.

n-Butyrylbenzenesulphanilide, $C_6H_5N<^{COCH_2CH_2CH_3}_{SO_2C_6H_5}$.—This compound, prepared in the same manner as the acetyl and propionyl compounds, gave stout prisms when crystallized from alcohol, melting at 89°–90°. Satisfactory measurements, for a crystallographic description, were not obtained. A nitrogen determination gave:

	Calculated for $C_{16}H_{17}NO_3S$.	Found.
N	4.62	4.38

Benzoylbenzenesulphanilide, $C_6H_5N<^{COC_6H_5}_{SO_2C_6H_5}$. — The crystals of this compound were small and well developed when grown from a dilute solution, not being more than 2 mm. in length. From more concentrated solutions it comes down in long, thin needles. It was found that the crystals of this compound were monoclinic but showed no hemimorphic or pyroelectric properties. When crystallized repeatedly from alcohol, they melt at 114°–115°, and a nitrogen determination gave the following results:

	Calculated for $C_{19}H_{15}NO_3S$.	Found.
N	4.15	4.29

The forms observed are:

b, 010 *c*, 001 *m*, 110 *l*, 120 *x*, $\bar{1}01$

The measurements obtained are the following:

		Measured.	Calculated.
$c \wedge x$,	$001 \wedge \bar{1}01 =$	*80° 18′	. . .
$c \wedge m$,	$001 \wedge 110 =$	*61° 50′	. . .
$m \wedge m$,	$1\bar{1}0 \wedge 110 =$	*68° 56′	. . .
$m \wedge l$,	$110 \wedge 120 =$	19° 26′	19° 27′
$c \wedge l$,	$001 \wedge 120 =$	70° 19′	70° 17′
$m \wedge x$,	$110 \wedge 10\bar{1} =$	54° 3′	54° 5′
$l \wedge x$,	$120 \wedge 10\bar{1} =$	64° 34′	65° 0′

Axes $a : b : c : = 0.8373 : 1 : 1.175$. $\beta = 100 \wedge 001 = 55° 4'$.

Fig. 5 represents the prevailing habit of benzoylbenzenesulphanilide. No close crystallographic relation was found between this compound and the preceding ones.

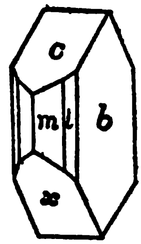


Fig. 5.

A small quantity of the above compound was heated in a test-tube to 180°. Dry hydrogen chloride was passed in and benzoyl chloride was formed. When the diacyl anilide was heated with benzoyl chloride to 180° for ten hours, a reddish oil was obtained, which solidified on cooling. This was crystallized from alcohol, when a mass of colorless needles was obtained, melting from 160°–161°. A nitrogen determination gave 4.93 per cent of nitrogen, while the calculated percentages for benzanilide and dibenzanilide are 7.07 and 4.65, respectively. The material formed by this treatment was therefore dibenzanilide.

Benzenesulph-a-naphthalide, $C_{10}H_7NHSO_2C_6H_5$. — This was obtained by the Baumann-Schotten reaction in the usual manner. When crystallized from alcohol it separated in needles and melted at 168°–169°. A nitrogen determination gave:

	Calculated for $C_{16}H_{13}NO_2S$.	Found.
N	4.94	4.47

Benzoylbenzenesulph-a-naphthalide, $C_{10}H_7N{<}{\genfrac{}{}{0pt}{}{COC_6H_5}{SO_2C_6H_5}}$.—The crude material in this case was purified by boiling with absolute alcohol, washing with sodium hydrate, and then crystallizing from a mixture of benzene and ligroïn. It formed minute crystals, which melted constantly at 193°–194°, and which seemed to be pure. Nitrogen determinations in different samples, however, invariably came low.

	Calculated for $C_{23}H_{17}NO_3S$.	Found. I.	II.	III.	IV.
N . . .	3.61	2.78	3.05	2.72	2.90

Benzenesulph-β-naphthalide, $C_{10}H_7NHSO_2C_6H_5$. — This material crystallized poorly from dilute alcohol in small, oblong

plates or flattened prisms, which apparently melted constantly at 97°.

	Calculated for $C_{15}H_{15}NO_3S$.	Found.
N	4.9	4.7

Benzoylbenzenesulph-β-naphthalide, $C_{10}H_7N<\begin{matrix}COC_6H_5\\ SO_2C_6H_5\end{matrix}$.—This consisted of minute, fine, white needles, melting at 161°–162.°

	Calculated for $C_{23}H_{17}NO_3S$.	Found.
N	3.6	3.4

Formanilide, C_6H_5NHCHO.—The crystals for examination in this case were prepared by spontaneous evaporation of a solution of the anilide in a mixture of low-boiling ligroïn and ether. This gave monoclinic crystals about 6 or 7 mm. in length, and the following forms were observed:

a, 100 *c*, 001 *e*, 101 *d*, 011 *p*, 112

The measurements obtained were as follows:

	Measured.	Calculated.
$c \wedge e$, $001 \wedge 101 =$	*26° 17′	. . .
$a \wedge c$, $100 \wedge 001 =$	*85° 6′	. . .
$c \wedge d$, $001 \wedge 011 =$	67° 20′	. . .
$a \wedge e$, $100 \wedge 101 =$	58° 52′	58° 49′
$d \wedge d$, $011 \wedge 01\bar{1} =$	45° 24′	45° 20′
$a \wedge d$, $100 \wedge 011 =$	87° 57′	88° 6′
$e \wedge d$, $101 \wedge 011 =$	80° $8\frac{1}{2}$′	80° $10\frac{1}{2}$′
$p \wedge p$, $112 \wedge \bar{1}1\bar{2} =$	83° 8′	83° 0′

Axes $= a : b : c = 2.188 : 1 : 2.403$. $\beta = 100 \wedge 001 = 85° 6'$.

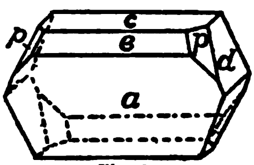


Fig. 6.

The crystals of formanilide were for the most part imperfect and gave poor reflections. Acetanilide has been measured by Bücking,* and was found to be orthorhombic, the axes $a : c = 0.848 : 2.067$.

NEW HAVEN, May, 1897.

* Jahresb., 1877, 679.

NOTE ON DOUBLE SALTS OF THE ANILIDES WITH CUPROUS CHLORIDE AND CUPROUS BROMIDE.*

By WILLIAM J. COMSTOCK.

In studying the behavior of certain "Schiff bases" toward cuprous chloride and cuprous bromide, it seemed to me desirable to find derivatives of the cuprous halides which should be soluble in organic solvents and give up the halides easily. In looking for such derivatives, I found the acetanilide salts here described. As the anilides enter so few combinations in which the basic character of the nitrogen appears, it seems worth while to show that acetanilide is not an exceptional case. The formyl compounds give similar double salts with the greatest ease, but the formyl group splits off so easily under the condition necessary for their formation, that accurate analytical results are difficult to obtain. For instance, when formanilide is added to a solution of cuprous bromide in a mixture of formic and hydrobromic acids, there is formed at once a salt crystallizing beautifully in well-developed, colorless, doubly terminated prisms. On standing for but a few minutes at ordinary temperature, a change into small plates with very noticeable pearly lustre, can be observed. These plates consist of the double salt of aniline with cuprous bromide, $C_6H_5NH_2HBrCuBr$. The corresponding salt of formparatoluide was, however, obtained, and gave on analysis sufficiently accurate results.

An interesting series of perhalides of the anilides has been carefully studied in this laboratory by Wheeler and Walden.† It will be seen that the salts here described,

* Amer. Chem. Jour., xx, No. 1.
† Ibid., xviii, 85.

$(\text{Anilide})_2$ + HBr + CuBr, and $(\text{anilide})_2$ + HBr + 2CuBr, correspond to two of the three types of perhalides obtained by the above-mentioned investigators.

Experimental.

$(C_6H_5NH.COCH_3)_2HClCuCl$. — An advantageous solution for the preparation of this salt consists of a mixture of one volume of glacial acetic acid, one volume of strong hydrochloric acid, and two volumes of water. The acetanilide and cuprous chloride are dissolved in the hot mixture in the proportion indicated in the above formula. On cooling, the solution solidifies to a mass of long, thin, white prisms. When freshly prepared and not quite dry, the salt dissolves easily in alcohol, crystallizing in beautiful, long prisms, when the hot concentrated solution is allowed to cool slowly. This complete solution in alcohol is doubtless due to the small quantity of hydrochloric acid which has not yet been removed, as the perfectly dry salt always leaves a small residue of cuprous chloride when treated with alcohol. However, many grams of the dried substance will form a clear solution in alcohol to which a few drops of dilute hydrochloric acid are addded. Methyl alcohol and acetone can also be used for recrystallizing it. Protracted boiling of the solution splits off the acetyl group. The compound has no sharp melting-point. When heated slowly it darkens at about 140°; complete fusion, accompanied by violent decomposition, takes place near 170°. Freshly prepared it is entirely colorless, but it usually has a faint yellow color by the time it is dry, especially when prepared in quantity. When dry it is quite stable, and can be kept for months with no change of color, unless exposed to moist air. It does not lose hydrochloric acid *in vacuo* over potassium hydroxide, and when dry can be heated to 100° without loss of weight. The following analytical results were obtained:

	Calculated for above composition.	Found. I.	Found. II.
Cu	15.64	15.73	15.77
Cl	17.51	17.50	17.47

$(C_6H_5NHCOCH_3)_2HBr.CuBr.$—This salt can be prepared from its constituents by using a mixture of one volume glacial acetic acid, one volume hydrobromic acid (sp. gr. 1.49), and two volumes of water. More advantageous, however, is the preparation in alcoholic solution. The anilide and bromide are used in theoretical proportion, the hydrobromic acid in slight excess. Sufficient alcohol is used to effect complete solution at the boiling-point, and the hot solution cooled slowly. The salt separates in long, colorless, doubly-terminated prisms. Similarly to the cuprous chloride salt, it dissolves completely in alcohol, methyl alcohol, and acetone, if a drop of hydrobromic acid is added. While drying, the crystals show temporarily on the surface that purple color so characteristic of copper compounds in presence of strong hydrobromic acid; but when dry they have at most a light grayish color. The dried salt is fully as stable as the corresponding chloride. On heating, it begins to darken at about 170°, and melts with decomposition from 185° to 195°, according to the rapidity of heating. Analysis gave the following results:

	Calculated.	Found. I.	Found. II.
Cu . . .	12.82	13.29	13.20
Br . . .	32.36	32.39	32.41

$\left(C_6H_4<^{Br}_{NHCOCH_3}\right)_2HBrCuBr.$—Parabromacetanilide gives with cuprous bromide a double salt of the above composition. The compound separates in long, colorless prisms, on cooling a hot solution of the constituents dissolved in a mixture of two volumes of alcohol and one volume of hydrobromic acid (sp. gr. 1.49). The substance thus prepared and dried *in vacuo* over sulphuric acid and potassium hydroxide, was used for a copper estimation, which gave 9.79 per cent copper. For the above composition the theory requires 9.72 per cent copper

Formparatoluide and Cuprous Bromide.

$\left(C_6H_4<^{CH_3}_{NHCHO}\right)_2HBr.2CuBr.$—This salt must be prepared in the cold and dried quickly. 3 g. of formparatoluide

dissolved in 12 c. c. of formic acid (sp. gr. 1.20) were added to a solution of 3 g. of cuprous bromide dissolved in 24 c. c. dilute hydrobromic (one volume HBr, sp. gr. 1.49, to one volume water). The salt separated at once in colorless, flat prisms. It was dried on a porous plate, then *in vacuo* over sulphuric acid and potassium hydroxide. It gave the following results on analysis:

	Calculated.	Found. I.	Found. II.
Cu . . .	19.88	19.57	19.68
Br . . .	37.63	37.47	. . .

ON ACYL IMIDO-ESTERS.*

SECOND PAPER.

By H. L. WHEELER, P. T. WALDEN, and H. F. METCALF.

In a previous paper, by two of us, it was shown that the imidomethyl and ethyl benzoates give acyl derivatives with acetyl and benzoyl chloride, the reaction taking place as follows:

$$2C_6H_5C\left\langle\begin{matrix}NH\\OCH_3\end{matrix}\right. + ClCOCH_3 = C_6H_5C\left\langle\begin{matrix}NCOCH_3\\OCH_3\end{matrix}\right. + C_6H_5C\left\langle\begin{matrix}NH_2\\Cl\\OCH_3\end{matrix}\right.$$

Two molecules of the imido-ester react with one molecule of acyl chloride, giving one molecule of acyl imido-ester and one molecule of the imido-ester hydrochloride.

We now find that the acyl imido-esters may also be prepared from the silver salts of diacyl amides. Silver dibenzamide gave, with ethyl iodide, a product identical in every respect with that obtained from benzimidoethyl ester and benzoyl chloride; *i. e.*, $C_6H_5C\left\langle\begin{matrix}NCOC_6H_5\\OC_2H_5\end{matrix}\right.$. The product had entirely different properties from those of the isomeric nitrogen ethyl compound, $C_6H_5CON(C_2H_5)COC_6H_5$, which was prepared from ethylbenzamide. The reaction, therefore, takes place as follows:

$$C_6H_5C\left\langle\begin{matrix}NCOC_6H_5\\OAg\end{matrix}\right. + IC_2H_5 = C_6H_5C\left\langle\begin{matrix}NCOC_6H_5\\OC_2H_5\end{matrix}\right. + AgI.$$

The behavior of the silver salts of diacyl amides towards

* Amer. Chem. Jour., xx, No 1, January, 1898.

ethyl iodide is thus shown to be perfectly analogous to that of the silver salts of monoacylamides * and anilides. †

The acyl imido-esters are very reactive substances, and it was with difficulty that some were obtained in a state of approximate purity. They react with water, immediately in the presence of acids, in either of two ways; *i. e.*, alcohol is separated, and a diacylamide results, or a monoacylamide and an ester are formed. These decompositions may be represented as follows:

$$C_6H_5C\begin{matrix} \diagup\!\!\!\diagup NCOC_6H_5 \\ \diagdown OCH_3 \end{matrix} + H_2O = C_6H_5C\begin{matrix} \diagup N<^{COC_6H_5}_{H} \\ -O\vdots H \\ \diagdown \vdots OCH_3 \end{matrix}$$

As far as observed, the acetyl, propionyl, butyryl, carbethoxyl, and benzoylbenzimido esters behave in the above manner, while benzoylphenylacetimidoethyl ester and those imido-esters containing the acyl group, $-COCO.OC_2H_5$, do not give diacyl amides, but readily decompose as follows:

$$C_6H_5CH_2C\begin{matrix} \diagup\!\!\!\diagup NCOC_6H_5 \\ \diagdown OC_2H_5 \end{matrix} + H_2O = C_6H_5CH_2C\begin{matrix} \diagup \vdots N<^{COC_6H_5}_{H} \\ -O\vdots H \\ \diagdown OC_2H_5 \end{matrix}$$

These reactions show conclusively that the diacyl amides have both acyl groups attached to nitrogen.

To what extent the acyl imido-esters decompose according to the first representation, otherwise than indicated above, remains to be investigated. At present this decomposition suggests an easy method for the preparation of certain diacyl amides, it being only necessary to treat the reaction-product of an acyl chloride and an imido-ester, with hydrochloric acid, when the diacyl amide immediately separates pure and in crystalline form.

The instability of the acyl imido-esters in the presence of moisture, acids, etc., recalls the similar behavior of the oxy-

* Tafel and Enoch, Ber. d. chem. Ges., xxiii, 104.

† Comstock and Kleeberg, Ibid., xii, 493.

gen ethers of succinimide,* which readily separate alcohol and revert to succinimide. The grouping $RC\begin{array}{l}\diagup\!\!\diagup NR' \\ \diagdown OC_2H_5\end{array}$ becomes less stable in the presence of moisture as the negative character of the groups R and R′ are increased.

When benzoylbenzimidoethyl ester is heated with benzoyl chloride, it reacts slowly and tribenzamide results:

$$C_6H_5C\begin{array}{l}\diagup\!\!\diagup NCOC_6H_5 \\ \diagdown OC_2H_5\end{array} + ClCOC_6H_5 = C_6H_5C\begin{array}{l}\diagup N<\begin{array}{l}COC_6H_5\\ COC_6H_5\end{array} \\ -Cl \\ \diagdown OC_2H_5\end{array}$$

This reaction is analogous to the action of acyl chlorides on the isoanilides,† in which case diacylanilides were formed. It therefore indicates that in the triacylamides all three acyl groups are attached to nitrogen. An attempt was made to determine the structure of the triacylamides and to prove the equivalence of the three bounds of nitrogen, in respect to acyl groups, by allowing benzoyl chloride to react on acetylbenzimidoethyl ester, on the one hand, and acetyl chloride on benzoylbenzimidopropyl ester on the other. Tribenzamide, however, was formed in the first case while, in the second, nothing but decomposition-products were observed.

When the acyl imido-esters are treated with ammonia or bases, acylamidines are formed:

$$C_6H_5C\begin{array}{l}\diagup\!\!\diagup NCOC_6H_5 \\ \diagdown OC_2H_5\end{array} + H_2NR = C_6H_5C\begin{array}{l}\diagup N<\begin{array}{l}COC_6H_5\\ H\end{array} \\ -OC_2H_5 \\ \diagdown NHR\end{array}.$$

The structure of these cannot be determined by their method of formation since the above hypothetical addition-product can give up alcohol in two ways, giving either

$$C_6H_5C\begin{array}{l}\diagup\!\!\diagup NCOC_6H_5 \\ \diagdown NHR\end{array} \quad \text{or} \quad C_6H_5C\begin{array}{l}\diagup NHCOC_6H_5 \\ \diagdown\!\!\diagdown NR\end{array}.$$

* Comstock and Wheeler, Amer. Chem. Jour., xiii, 519.

† Wheeler and Walden, Ibid., xix, 129.

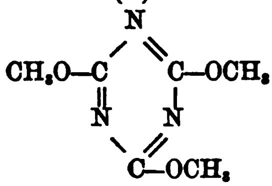
The acylamidines will be described in a later paper.

When benzoylbenzimidioethyl ester was heated in a stream of dry ammonia, the following decomposition was observed:

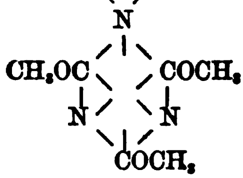
$$C_6H_5C\left\langle\begin{matrix}N\,\boxed{COC_6H_5\\OC_2H_5 + NH_3}\end{matrix}\right. = C_6H_5CN + C_6H_5CONH_2 + C_2H_5OH.$$

The violence with which acyl chlorides, but especially acetyl chloride, react with the imido-esters, isoanilides, or compounds containing the arrangement $RC\left\langle\begin{matrix}NR'\\OR''\end{matrix}\right.$, in which the radical *R'* is not a negative (acyl) group, suggests that it would be of interest to compare the behavior of some rings supposed to contain this grouping. At present we have tried the trimethyl ester of normal cyanuric acid. This, if constituted as described in the text-books, formula (A), contains three of the above groups and should react, giving the triacetyltricarbonimide of Ponomarew.*

(A).



(B).



The trimethyl ester was prepared by the directions of Hofmann † from cyanuric chloride and sodium methylate. It was then found that this ester can be crystallized unaltered from acetyl chloride, and no action at the boiling-point of acetyl chloride was observed. It seems, therefore, improbable that there are three double unions in the normal cyanuric esters, or, which is practically the same, that they contain para bonds. The inertness of this ester, however, might be explained by the centric formula (B), or it may be due to the ring formation. It is our intention to continue this work on

* Ber. d. chem. Ges., xviii, 3275.

† Ibid., xix, 2063.

the action of acyl chlorides on ring-formed compounds which, theoretically, may be considered as derived from the grouping $RC\begin{smallmatrix}\diagup\!\!\diagup NR' \\ \diagdown OR''\end{smallmatrix}$.

Experimental Part.

Benzimidomethyl Ester, $C_6H_5C\begin{smallmatrix}\diagup\!\!\diagup NH \\ \diagdown OCH_3\end{smallmatrix}$.—For the preparation of acyl imido-esters, freshly prepared and distilled imido-esters were used. The imido-ester hydrochlorides were prepared by Pinner's well-known method, and the free esters according to Bushong's directions.*

This compound boiled at 96° under a pressure of 13 mm. Bushong found it to boil at 96° at 10 mm. In a previous paper † it was stated that benzimidomethyl ester deposits benzamide on standing. This is not the case when the ester is prepared from benzonitrile by the method of Pinner, and then distilled. The pure ester may be kept for months without any apparent change. A specimen exposed in a test-tube plugged with cotton, after standing a year, deposited a few crystals. These melted at 230°, and were, therefore, cyanphenine.

The Picrate, $C_6H_5C\begin{smallmatrix}\diagup\!\!\diagup NH \\ \diagdown OCH_3\end{smallmatrix}.C_6H_2(NO_2)_3OH$.—An alcoholic solution of picric acid added to benzimidomethyl ester in ether gives a heavy, lemon-yellow, crystalline precipitate. This melts at 163°, and from alcohol or water it forms stout prisms. A nitrogen determination gave:

	Calculated for $C_{14}H_{12}N_4O_8$.	Found.
N	15.38	15.06

Benzoylbenzimidomethyl Ester, $C_6H_5C\begin{smallmatrix}\diagup\!\!\diagup NCOC_6H_5 \\ \diagdown OCH_3\end{smallmatrix}$.—When benzoyl chloride is mixed with benzimidomethyl ester in ethereal solution, in the proportion of one molecule of the former to two of the latter, the reaction is practically complete

* Amer. Chem. Jour., xviii, 490.

† Ibid., xvii, 398.

in twenty-four hours. It was found advisable to treat the reaction-product here, as in most of the other cases, as follows: On filtering from the imido-ester hydrochloride, the ether solution was shaken with dilute alkali, dried over solid potassium hydrate, then calcium chloride, and finally, on evaporating off the ether, the products were usually obtained as oils. This compound, unlike the corresponding ethyl and isobutyl derivatives, refused to solidify without decomposition. It was found to boil from 210° to 212° at 12 mm. pressure. A nitrogen determination in the colorless oil thus obtained gave:

	Calculated for $C_{10}H_{13}NO_2$.	Found.
N	5.8	5.5

When benzoylbenzimidomethyl ester is treated with a drop of hydrochloric acid in alcoholic solution, dibenzamide separates. Dibenzamide is also deposited when the material is allowed to stand.

Carbethoxylbenzimidomethyl Ester, $C_6H_5C\begin{matrix}/\!\!/ NCO_2C_2H_5 \\ \diagdown OCH_3\end{matrix}$.—Benzimidomethyl ester and chlorcarbonic ethyl ester were boiled in ethereal solution for a number of hours. On cooling the ethereal solution, plates separated. These melted at about 126° and on crystallizing from water melted at 128°. This material proved to be benzamide. The ether was evaporated, and a mixture of oil and crystals of benzamide obtained; on distilling this at 14 mm. it was found to boil from 148° to 156°. This fraction was treated with a mixture of equal volumes of ether and ligroïn, filtered from precipitated benzamide, and then, after evaporating the solvent, a colorless oil was obtained which boiled at 155° at 14 mm. pressure. A nitrogen determination gave the following result:

	Calculated for $C_{11}H_{13}NO_3$.	Found.
N	6.7	6.9

Benzoylurethane, $C_6H_5CONHCO_2C_2H_5$.—A few drops of the above material were treated with cold dilute hydrochloric acid,

the mass then solidified, and, on washing with water, it melted from 110° to 111°. This solid dissolved readily in dilute sodium hydroxide, and was precipitated unaltered by dilute hydrochloric acid. It had all the properties of benzoylurethane, as described by Pechmann.*

Ethyloxalylbenzimidomethyl Ester, $C_6H_5C\langle{}^{NCOCO_2C_2H_5}_{OCH_3}$.— 7.7 g. of ethyl chloroxalate were slowly dropped into 15.4 g. of benzimidomethyl ester, largely diluted with dry ether. The reaction is violent and is complete when the ester is all added. On filtering and evaporating the ether a clear colorless oil was obtained. This was distilled at 23 mm. pressure. Below 206° a few drops collected, the latter portion of which solidified in flattened prisms, which melted at 114°–115° and proved to be oxamethane. From 206° to 207° a thick syrup distilled over, which constituted almost the entire portion. It was redistilled at 14 mm., when it boiled at 192°. The latter portion of this distillate gave on analysis:

	Calculated for $C_{12}H_{13}NO_4$.	Found.
N	5.95	6.21

When ethyloxalylbenzimidomethyl ester is exposed to the air for some time, or when boiled with water, the odor of benzoic ester is noticed and oxamethane results. The formation of benzoyloxamethane was not observed in this case, the decomposition taking place according to the second method mentioned in the introduction. Concentrated aqueous ammonia immediately decomposes this acyl imido-ester into oxamide and methyl benzoate. It soon solidifies when mixed with aniline.

Benzimidoethyl Ester, $C_6H_5C\langle{}^{NH}_{OC_2H_5}$. — This was prepared by the method of Pinner. It was observed to distil at 101°–102° at 15 mm. pressure. Bushong † gives its boiling-point as 106°–109° at 15 mm.

* Ber. d. chem. Ges., xxviii, 2383.

† Loc. cit.

Benzimidoethylester Mercuric Chloride, $C_6H_5C\begin{cases}NH.HgCl\\ Cl\\ OC_2H_5\end{cases}$.—Not only do the imido-esters give well-crystallized addition-products with picric acid, but also in some cases with mercuric chloride. The above was prepared by adding benzimidoethyl ester to an alcoholic solution of mercuric chloride. The addition-product then separates in a mass of colorless needles. It was recrystallized from ether, and a chlorine determination gave the following result:

	Calculated for $C_9H_{11}NOHgCl_2$.	Found.
Cl	16.9	16.9

Acetylbenzimidoethyl Ester, $C_6H_5C\begin{cases}NCOCH_3\\ OC_2H_5\end{cases}$.—This compound we described in a previous paper. We have now prepared it in larger quantities, and find its boiling-point to be 156° at 17 mm. instead of 151°.

When acetylbenzimidoethyl ester is mixed with benzoyl chloride, and the mixture kept at a temperature of 100°–120° for a number of hours, a mass of needles separates. This proved to be tribenzamide.

Propionylbenzimidoethyl Ester, $C_6H_5C\begin{cases}NCOC_2H_5\\ OC_2H_5\end{cases}$.—The mixture in this case was allowed to stand for twenty-four hours, and then treated as in the case of benzoylbenzimidomethyl ester. The product was an oil which, on fractioning, boiled between 161° and 162° at 17 mm. pressure. A nitrogen determination gave:

	Calculated for $C_{12}H_{15}NO_2$.	Found.
N	6.83	7.08

Propionylbenzamide, $CH_3CH_2CO.NHCOC_6H_5$.—When the ethereal solution of propionylbenzimidoethyl ester is shaken with a few drops of concentrated hydrochloric acid, and the ether evaporated, this diacyl amide separates in the form of needles or prisms. Crystallized from alcohol, it melts at 98°. A nitrogen determination gave:

	Calculated for $C_{10}H_{11}NO_2$.	Found.
N	7.91	8.08

Normal Butyrylbenzimidoethyl Ester, $C_6H_5C\begin{matrix}\diagup\!\!\diagup NCOC_3H_7 \\ \diagdown OC_2H_5\end{matrix}$. — Normal butyryl chloride produces an immediate precipitate when added to benzimidoethyl ester dissolved in ether. The mixture was allowed to stand twenty-four hours, and then treated as in the case of benzoylbenzimidomethyl ester. The product was an oil which, on fractioning, boiled at 167° at 16 mm. pressure. A nitrogen determination gave:

	Calculated for $C_{13}H_{17}NO_2$.	Found.
N	6.39	6.64

Normal Butyrylbenzamide, $C_3H_7CO.NH.COC_6H_5$. — On shaking the ethereal solution of the above acyl imido-ester with concentrated hydrochloric acid, this compound separates in the form of beautiful colorless prisms. These, after three crystallizations from alcohol, melted constantly at 104°–105°. A nitrogen determination gave:

	Calculated for $C_{11}H_{13}NO_2$.	Found.
N	7.33	7.96

Benzoylbenzimidoethyl Ester, $C_6H_5C\begin{matrix}\diagup\!\!\diagup NCOC_6H_5 \\ \diagdown OC_2H_5\end{matrix}$. — This acyl imido-ester is the easiest to obtain in the solid condition, and therefore probably purer than the corresponding benzoylbenzimidomethyl and propyl esters, which were obtained only in the form of oils. In addition to the method already given, this compound was prepared from silver dibenzamide, as follows: 12 g. of the silver salt, dried at 100°, were suspended in ether and boiled with an excess of ethyl iodide. After several hours the ether, on evaporation, gave an oil, which soon solidified, giving the characteristic lozenge-shaped crystals melting at 65°. Sulphuric acid converted the material into dibenzamide.

Tribenzamide, $(C_6H_5CO)_3N$. — 4 g. of the above compound were heated with 2.2 g. of benzoyl chloride. Little or no reaction took place below 100°, and even at 130°–150° the evolution of gas (ethyl chloride) was slow. After several hours crystals were obtained. These, when crystallized from alcohol, melted at about 202°, and were, therefore, tribenzamide. A nitrogen determination gave:

	Calculated for $C_{21}H_{15}NO_3$.	Found.
N	4.25	4.39

Ethyldibenzamide, $(C_6H_5CO)_2NC_2H_5$. — For the preparation of this compound, which is isomeric with benzoylbenzimidoethyl ester, we wish to express our thanks to Mr. T. E. Smith. He prepared this amide as follows: Ethylbenzamide was prepared by the Baumann-Schotten method. The sodium salt of this, suspended in toluene with benzoic anhydride, gave ethyldibenzamide. The product thus obtained crystallized from alcohol in colorless prisms, melting at 101°–102°. A nitrogen determination gave:

	Calculated for $C_{16}H_{15}NO_2$.	Found.
N	4.9	5.2

Ethyloxalylbenzimidoethyl Ester, $C_6H_5C\begin{matrix}\nearrow NCOCO_2C_2H_5 \\ \searrow OC_2H_5\end{matrix}$. — Ethyl chloroxalate reacts violently when mixed with benzimidoethyl ester dissolved in ether. The product is an oil which, on fractioning, boils from 190° to 195° at 11 mm. pressure. The crude material generally contains oxamethane, which distils over in the first portions. An analysis of the above fraction gave the following result:

	Calculated for $C_{13}H_{15}NO_4$.	Found.
N	5.8	6.0

This material readily decomposes into oxamethane and ethyl benzoate. The formation of benzoyloxamethane was not observed.

Benzimido(normal)propyl Ester, $C_6H_5C{\begin{smallmatrix}\nearrow NH \\ \searrow OCH_2CH_2CH_3\end{smallmatrix}}$. — Pinner does not mention this imido-ester in his work "Die Imidoäther und ihre Derivate." We obtained it as a colorless, pleasant-smelling oil, which boiled unaltered at 115.5° at 12 mm. pressure, and at 232° at 765 mm. pressure.

	Calculated for $C_{10}H_{13}NO$.	Found.
N	8.59	8.59

The hydrochloride melts at 125°, giving off ethyl chloride and forming benzamide.

	Calculated for $C_{10}H_{13}NO.HCl$.	Found.
Cl	17.79	17.77

The picrate, obtained in the same manner as the corresponding methyl ester derivative, forms lemon-yellow prisms, which melt with charring at 261°, or 98° higher than the picrate of benzimidomethyl ester.

Acetylbenzimido(normal)propyl Ester, $C_6H_5C{\begin{smallmatrix}\nearrow NCOCH_3 \\ \searrow OCH_2CH_2CH_3\end{smallmatrix}}$. — When acetyl chloride is added to the imido-ester in ether, the separation of hydrochloride begins at once. The mixture was allowed to stand twelve hours, the ether solution was shaken with dilute sodium hydrate, and, on drying and evaporating, an oil was obtained. This was distilled at 12 mm. pressure, and the fraction boiling from 153° to 160° was redistilled, when the main portion boiled at 153° at 13 mm. pressure. A nitrogen determination gave:

	Calculated for $C_{12}H_{15}NO_2$.	Found.
N	6.83	6.79

When this acyl imido-ester is exposed to the air or treated with acids, it deposits acetbenzamide.

Benzoylbenzimido(normal)propyl Ester,

$$C_6H_5C{\begin{smallmatrix}\nearrow NCOC_6H_5 \\ \searrow OCH_2CH_2CH_3\end{smallmatrix}}. —$$

— This compound was obtained in the form of an oil which was distilled at 17 mm. pressure; the portion boiling from 231° to 232.5° was analyzed with the following result:

	Calculated for $C_{17}H_{17}NO_2$.	Found.
N	5.24	5.20

When treated with dilute hydrochloric acid, it gave dibenzamide.

Benzimidoisobutyl Ester, $C_6H_5C\begin{smallmatrix}\nearrow NH\\ \searrow OC_4H_9\end{smallmatrix}$. — Pinner found that when this imido-ester is liberated from the hydrochloric acid salt, by means of ammonia, and then a distillation is attempted, it is largely decomposed. We have found that if it is liberated by means of a ten per cent solution of ice-cold sodium hydroxide, and then distilled under diminished pressure, it can afterward be distilled at ordinary pressures without the slightest decomposition. It was observed to boil at 9 mm. pressure at 117.5° to 120°, and at ordinary pressure from 248° to 250°. It gives an oily precipitate with alcoholic mercuric chloride, which finally solidifies.

Benzoylbenzimidoisobutyl Ester, $C_6H_5C\begin{smallmatrix}\nearrow NCOC_6H_5\\ \searrow OC_4H_9\end{smallmatrix}$. — The product in this case was an oil which, when distilled at 15 mm. pressure, boiled from 228° to 235°. The distillate easily solidified and, on crystallizing from ligroïn, it melted constantly at 54.5°.

	Calculated for $C_{18}H_{19}NO_2$.	Found.
N	4.9	4.9

Phenylacetimidomethyl Ester, $C_6H_5CH_2C\begin{smallmatrix}\nearrow NH\\ \searrow OCH_3\end{smallmatrix}$. — The hydrochloride of this imido-ester was prepared by Pinner. He does not mention the free base. When prepared as stated in the case of benzimidoisobutyl ester, it gave a pleasant-smelling oil, which distilled at 114.5°–115° at 20 mm. pressure.

Phenylacetimidoethyl Ester, $C_6H_5CH_2C\begin{smallmatrix}\nearrow NH\\ \searrow OC_2H_5\end{smallmatrix}$. — It was found that this ester could be distilled under diminished pressure. It boiled at 116° at 15 mm. pressure. On attempting then to distil it at ordinary pressure it decomposed into alcohol and the nitrile.

Benzoylphenylacetimidoethyl Ester, $C_6H_5CH_2C\begin{matrix}\diagup\!\!\!\diagup NCOC_6H_5 \\ \diagdown OC_2H_5\end{matrix}$. —This was obtained as an oil which did not solidify without decomposition. It boils from 215° to 216° at 13 mm. pressure.

	Calculated for $C_{17}H_{17}NO_2$.	Found.
N	5.2	5.9

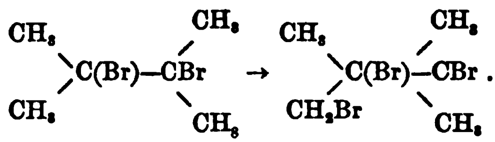
In one attempt to prepare the above, a mass of plates separated on evaporating the ether solution. These melted at 128° and contained 11.31 per cent nitrogen; calculated for benzamide, 11.56. The compound, therefore, readily decomposes into benzamide and phenyl ethyl acetate. The above analyzed material evidently contained some benzamide, which explains the high result for nitrogen.

NEW HAVEN, November, 1897.

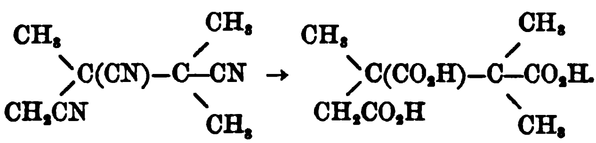
ON SOME BROMINE DERIVATIVES OF 2,3-DIMETHYLBUTANE.*

By H. L. WHEELER.

THEORETICALLY by the action of one molecule of bromine on tetramethylethylene bromide or 2,3-dibrom-2,3-dimethylbutane, 2,3,K^3-tribrom-2,3-dimethylbutane should result as follows:



It is immaterial which hydrogen is substituted, as only one tribromide would result. Such a compound would be interesting on account of the possibility of converting it into the nitrile of camphoronic acid and this into the acid:



2,3-Dibrom-2,3-dimethylbutane is now readily prepared from pinacone by the methods of Baeyer † and Thiele. ‡

However, the action of one molecule of bromine on this compound, which is attacked with exceptional ease, does not give a tribromine compound, but, instead, a tetra derivative results and a corresponding amount of the material remains unaltered.

Linnemann § states that when isobutyl bromide is acted on by bromine, no trace of a dibromide is obtained, but a tri-

* Amer. Chem. Jour., xx, No. 2.

† Ber. d. chem. Ges., xxvi, 2563.

‡ Ibid., xxvii, 455.

§ Ann. Chem. (Liebig), clxii, 34.

bromide results exclusively. Linnemann's experiments were conducted at 150°. The author has found that, when this compound is brominated in the presence of iron, the reaction takes place readily on the steam-bath, and a dibromide results, although the yield is poor and the reaction is by no means as smooth as with ethyl and propyl bromides. This dibromide is apparently 1,2-dibrom-2-methylpropane. This result suggested the possibility of obtaining the tribromhexane by the use of iron. 2,3-Dibrom-2,3-dimethylbutane was therefore brominated with iron in carbon tetrachloride, but it was found that a tetrabromide results in this case also.

The product obtained without the use of iron melted constantly at 123° when crystallized from alcohol or ether. When, on the other hand, iron was present, a product melting at 139° was obtained. It was found later, by using carbon tetrachloride as a solvent, that the material melting at 123° was impure, and that it contained material melting at 139°–140°, and also a compound melting much higher. It was also found that a mixture of 2,3-dibrom-2,3-dimethylbutane melting at 192°, and the tetrabromide melting at 139° melts at about 123°. It is certain that the same tetrabromide results in both of the above cases. The products had apparently the same solubility, and the crystals were identical in appearance.

Bouchardat* obtained a tetrabromine derivative from iodhexylene by the action of bromine. This iodhexylene was prepared from pinacone hydrate and hydrogen iodide. He assigns the melting-point 142° to this compound.

It is probable that Bouchardat's product, melting at 142°, and that of the author, melting at 139°, are identical, especially since in both cases the same compound would be expected.

Mariuza † prepared a tetrabromhexane from di-isopropenyl, (2,3-dimethyl-1,3-butadiën) and bromine. This, Beilstein ‡ states, melts at 131°, and Couturier § confirms the preparation of a crystalline tetrabromide from this compound, but does not state its melting-point.

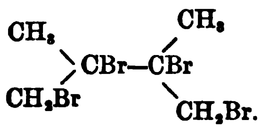
* Compt. rend., lxxiv, 810.

† Jour. Russ. Chem. Soc., xxi, 435.

‡ The original article is inaccessible to me.

§ Bull. Soc. Chim. (Paris), [3], iv, 30.

By the action of alcoholic potassium hydroxide on 2,3-dibrom-2,3-dimethylbutane the author has obtained an oil (2,3-dimethyl-1,3-butadiën), which on adding bromine gave a tetrabromide. This, on crystallizing from alcohol and ether, did not melt at 131° but at 139°. From the method of preparation it is concluded that this is identical with Mariuza's compound. It is identical in every respect with the product obtained by brominating 2,3-dibrom-2,3-dimethylbutane. Therefore this compound, the only tetrabromide of 2,3-dimethylbutane known at present, is 2,3,K^2,K^3-tetrabrom-2,3-dimethylbutane, and its structure is as follows:



(M. P. 139°).

Experimental Part.

2,3-Dibrom,2,3-dimethylbutane, $(CH_3)_2CBr-CBr(CH_3)_2$.—This was prepared by the method of Baeyer by saturating a glacial acetic acid solution of pinacone with hydrogen bromide, or by adding pinacone to hydrogen bromide solution saturated at 0° according to Thiele's directions. In both cases the product, on crystallizing from alcohol, melted at 192°, or thereabouts. There being some discrepancy in the statements regarding the melting-point of this compound, a bromine determination was made with the result given below. Pawlow * states that the compound melts at a temperature higher than 140°, Beilstein credits Eltekow † with the statement of 140° as its melting-point, and Kaschirsky ‡ 169°–170°, while Baeyer and Thiele do not mention its melting-point. Couturier § states that it melts at 171° in a closed tube, and Kondakow ‖ says that on keeping, the melting-point is reduced to 140°. This shows the influence that a slight impurity has on the melting-point of the substance.

* Ann. Chem. (Liebig), cxcvi, 124.
† Jour. Russ. Chem. Soc., x, 220.
‡ Ibid., xiii, 84.
§ Ann. Chem. et Phys. [6], xxvi, 433.
‖ J. prakt. Chem., liv, 431.

A bromine determination in a product prepared by Thiele's method, which melted at about 192°, gave the following:

	Calculated for $C_6H_{12}Br_2$.	Found.
Br	65.6	65.4

2,3-Dibrom-2,3-dimethylbutane, on being mixed with one molecular proportion of bromine, evolves a slow but steady stream of hydrogen bromide. After a number of hours, when the bromine practically disappears, the material washed with alcohol and crystallized from ether and alcohol — which removes some compound which attacks the eyes — melts then at 123°. A bromine determination gave:

	Calculated for $C_6H_{10}Br_4$.	Found.
Br	79.6	79.1

From ether, on spontaneous evaporation, beautiful minute prisms separated. These seemed to leave little doubt of the purity of the substance, but, on crystallizing from carbon tetrachloride the melting-point finally rose, and there was obtained a small amount of a substance crystallizing in needles and melting — not sharply — at 162° (Unaltered material ?). From the mother-liquor, on standing, needles and granular, stout prisms separated. The latter melted at 139°–140°.

Owing to the difficulty of purifying the material obtained in the above manner, attention was directed to the bromination in the presence of iron. This proceeds in a smoother manner and more rapidly.

2,3,K^2,K^3-*Tetrabrom-2,3-dimethylbutane.* — This was obtained when 25 g. of 2,3-dibrom-2,3-dimethylbutane (1 molecule), 0.5 g. iron wire and 18 g. of bromine (1 molecule + 1.4 g. Br for $FeBr_2$) were mixed in carbon tetrachloride. The mixture on warming begins to evolve hydrogen bromide, and then further warming is unnecessary. In a short time all the bromine disappears, and this compound separates in granular crystals melting at 139° (analysis I).

2,3-Dimethyl-1,3-butadiën, $CH_2{=}C(CH_3){-}C(CH_3){=}CH_2$. — An attempt was made to prepare 3-brom-2,3-dimethyl-1-

butene, $(CH_3)_2CBrC\begin{smallmatrix}\nearrow CH_3 \\ \searrow CH_2\end{smallmatrix}$, by the action of one molecule of alcoholic potassium hydrate on the dibromide. The mixture was boiled until it was no longer alkaline. It was then cooled, when unaltered dibromide separated, melting at 192°. The alcohol was distilled off and water was added to the distillate. This gave an oil which was dried over calcium chloride and distilled. The first and larger fraction boiled from 65° to 80°, and contained only a small amount of bromine, the remainder from 80° to 160°. When bromine was added to these fractions, in glacial acetic acid, an immediate precipitate of the tetrabromide melting at 139° was obtained. It was obtained in larger amount from the lower-boiling fraction. From the fact that the potassium hydroxide was neutralized in the above boiling, and that considerable unaltered material remained, it is concluded that this fraction is chiefly 2,3-dimethyl-1,3-butadiën, and that alcoholic potassium hydrate extracts 2 molecules of hydrogen bromide from 2,3-dibrom-2,3-dimethylbutane. This is confirmed by the fact that a tetra- and not a tribromide is obtained with bromine. A bromine determination in the case of the material melting at 139°, thus obtained, gave the following result (analysis II):

	Calculated for $C_6H_{10}Br_4$.	Found. I.	Found. II.
Br	79.6	79.5	80.0

1,2-Dibrom-2-methylpropane, $(CH_3)_2CBr—CH_2Br$. — When isobutyl bromide is warmed on the steam-bath with iron and bromine, in the proportion to form a dibromide, the reaction is complete in a short time. On washing the product with water and dilute sodium hydrate, an almost colorless oil was obtained. This dried over calcium chloride boiled from about 110° to 214°. On fractioning, a portion was obtained boiling from 146° to 151°, mostly between 148° and 149°; *i. e.*, the boiling-point of 1,2-dibrom-2-methylpropane. A bromine determination gave 70.8 per cent bromine instead of 74.0 per cent required for a dibromide. This material is therefore mostly 1,2-dibrom-2-methylpropane. From this it will be

noticed that bromine in the presence of iron acts on isobutyl bromide in the same manner as bromine acts on isobutyl iodide. Linnemann * states that in the latter case the yield is also poor.

When 2,3-dibrom-2,3-dimethylbutane was boiled with a slight excess of potassium hydrate, in alcoholic solution, an oil was obtained. This was dried over calcium chloride and inadvertently distilled over sodium. On adding bromine to the fraction boiling from 69° to 85°, *i. e.*, the larger fraction, a curious result was obtained. Regenerated 2,3-dibrom-2,3-dimethylbutane separated, melting at about 192°. This low-boiling fraction must, therefore, have contained 2,3-dimethyl-2-butene, which boils at 73°; $(CH_3)_2C{=}C(CH_3)_2$. This suggests that 2,3-dimethyl-1,3-butadiën, $CH_2{=}C(CH_3){-}C(CH_3){=}CH_2$, on partial reduction, does not give 2,3-dimethyl-1-butene, $(CH_3)_2CH{-}C(CH_3){=}CH_2$, but that a rearrangement takes place giving the above isomeric hydrocarbon. At present the lack of material prevents a further investigation of this subject.

New Haven, December, 1897.

* Loc. cit.

ON THE SILVER SALT OF 4-NITRO-2-AMINO-BENZOIC ACID, AND ITS BEHAVIOR WITH ALKYL AND ACYL HALIDES.*

By H. L. WHEELER and BAYARD BARNES.

It is well known, from the work of Griess,† Lauth,‡ Michler,§ Michael,|| and others, that the alkali salts of the aminobenzoic acids do not give esters directly with alkyl halides, but that the alkyl groups attach themselves entirely or partially to nitrogen. In this respect the sodium salts of the acyl amides and those of the aminobenzoic acids are analogous.

The silver salts of the amides, however, behave differently; ¶ here a replacement of the metal takes place and oxygen esters result, while the formation of nitrogen derivatives in this case has not been observed.

The action of alkyl and acyl halides on the silver salts of the aminobenzoic acids has, apparently, not been investigated, and it was with the object of investigating this action that the present work was undertaken. It seemed of interest to determine whether these silver salts behave like the silver salts of the amides and anilides, or whether, like the sodium compounds, the entering groups attach themselves to nitrogen.

The new 4-nitro-2-aminobenzoic acid was selected, as its esters are solids. We have found that the silver salt of this acid gives — as the chief product — with ethyl iodide in molecular proportions, 4-nitro-2-ethylaminobenzoic acid; the ethyl group attaching itself to nitrogen, and, next, in smaller quantity, 4-nitro-2-ethylaminoethyl benzoate is formed, while no 4-nitro-2-aminoethyl benzoate was observed.

* Amer. Chem. Jour., xx, No. 8.

† Ber. d. chem. Ges., v, 1038.

‡ Bull. Soc. Chim. (Paris) [3], ix, 970.

§ Ber. d. chem. Ges., ix, 401.

|| Amer. Chem. Jour., vii, 198.

¶ Comstock and Kleeberg, Ibid., xii, 493, and xiii, 514; Tafel and Enoch, Ber. d. chem. Ges., xxiii, 104 and 1554.

The behavior of the silver salt with ethyl iodide is therefore analogous to that of the above-mentioned sodium compounds. In this connection it may be remarked that Kraut * found that the silver salt of aminoacetic acid does not give the simple ester with ethyl iodide, when these compounds are used in molecular proportions, but the triethyl derivative of the ester, and in the same manner betaïn methyl ester results.

On the other hand, Curtius † found that the methyl and ethyl esters of acetyl glycin result from the silver salt, therefore the metal in this salt is directly replaceable. We have found, precisely in accordance with this, that if 4-nitro-2-aminobenzoic acid is acetylated, then both the sodium and silver salts give oxygen derivatives.

The action of acyl chlorides on the silver salt of anthranilic acid and on 4-nitro-2-aminobenzoic acid might lead to the formation of mixed anhydrides analogous to the action of acetyl chloride on sodium benzoate. ‡ We have found, however, that in the presence of the amino group the acyl group attaches itself entirely to nitrogen. A similar result was observed in the case of aminoacetic acid by Kraut,§ Hartmann,‖ and Curtius.¶ They prepared acetylaminoacetic acid from the silver salt of glycin and acetyl chloride, and Curtius showed that hippuric acid is thus formed. The silver salts of the anilides also give nitrogen derivatives with acyl halides.**

The sodium salts of the amides were formerly universally represented as having the metal attached to nitrogen, since they give nitrogen alkyl compounds with alkyl halides. As shown here, the silver salts of the aminobenzoic acids, which contain the metal joined to oxygen, nevertheless, give nitrogen derivatives with ethyl iodide, etc., and silver is generally more readily replaceable than sodium. It is shown from this, as has frequently been suggested, that the position of the metal in the salts of the amides cannot be determined by the

* Ann. Chem. (Liebig), clxxxii, 172. † Ber. d. chem. Ges., xvii, 1672.
‡ Gerhardt, Ann. Chem. (Liebig), lxxxvii, 81. § Loc. cit.
‖ Ann. Chem. (Liebig), cxxxiii, 105. ¶ J. prakt. Chem. [2], xxvi, 170.
** Wheeler and Boltwood, Amer. Chem. Jour., xviii, 381.

structure of the reaction-product, and that the sodium salts of the amides may have the metal joined to oxygen. If now, with this view, we arrange the salts of the amino and acetamino acids with those of the amide, according to their behavior with alkyl halides, we have the following:

$$\text{I.}\quad \begin{array}{l} NH_2 \\ | \\ CH_2CO_2Ag[Na] \end{array} \qquad \begin{array}{l} NH_2 \\ | \\ C_6H_4CO_2Ag[Na] \end{array} \qquad \begin{array}{c} NH \\ \| \\ RCONa \end{array}$$

$$\text{II.}\quad \begin{array}{l} NHCOCH_3 \\ | \\ CH_2CO_2Ag \end{array} \qquad \begin{array}{l} NHCOCH_3 \\ | \\ C_6H_4CO_2Ag \end{array} \qquad \begin{array}{c} NH \\ \| \\ RCOAg. \end{array}$$

The fact that the first series give nitrogen derivatives is explained by the positive character of the amido and imido groups; here the alkyl halide reacts by addition to the nitrogen, there being a subsequent separation of hydrogen halide, or, in the case of the amides, of sodium halide.

In the second series either these groups or the molecules are more negative, and additions to the nitrogen do not take place, but instead the metal is replaced by alkyl.

The above affords further data for and confirms the conclusion of Nef, Hantzsch,* Freer and Sherman,† and others, that the sodium in the salts of the amides and anilides is joined to oxygen. The amides and anilides, in general, have the normal structure, while the salts, with the possible exception of the mercury compounds, are derivatives of the pseudoform and contain the imido group. It is certain that most if not all the reactions of these compounds involve, as the first step, addition. These unstable addition-products then decompose into more stable derivatives, which latter constitute the products that are isolated.

Experimental Part.

4-Nitro-2-acetaminobenzoic Acid, $C_6H_3\begin{array}{l} \diagup CO_2H \quad (1) \\ -NHCOCH_3 \quad (2) \\ \diagdown NO_2 \quad (4) \end{array}$. — The acid was prepared by oxidizing 4-nitro-2-acettoluide

* Ann. Chem. (Liebig), ccxcvi, 91. † Amer. Chem. Jour., xviii, 570.

with a one per cent solution of potassium permanganate, the operation being essentially the same as that employed by Bedson * in oxidizing orthoacettoluide. Bedson obtained a yield of only 32 per cent of acetylorthoaminobenzoic acid. Apparently the nitroacettoluide is oxidized more smoothly, since we have obtained yields varying from 44 to 77 per cent of the calculated. The best yield is obtained when the quantity of toluide employed does not exceed 50 g. On filtering, concentrating, and acidifying the solution after oxidizing, the acid separates as a yellowish-white precipitate. It crystallizes from alcohol in long, light yellow needles, which melt at about 215°. A nitrogen determination gave:

	Calculated for $C_9H_8N_2O_5$.	Found.
N	12.5	12.4

It was observed that acids saponify this acetyl compound more readily than alkali.

The *sodium salt* was obtained as a bright yellow precipitate by adding one molecule of sodium ethylate to an absolute alcohol solution of the acid. It is readily soluble in water and somewhat in alcohol.

The *silver salt* is precipitated in a bright yellow, gelatinous form when silver nitrate is added to an aqueous solution of the sodium salt. It was found best to make the precipitation at a temperature of about 70°; then, on stirring vigorously, the precipitate becomes granular and is more readily filtered. It can be dried at 100°, and is quite stable when exposed to light.

	Calculated for $C_9H_7N_2O_5Ag$.	Found. I.	Found. II.
Ag . . .	32.6	32.35	32.31

Ethyl 4-Nitro-2-acetaminobenzoate was prepared by heating the above sodium salt with an excess of ethyl iodide in a sealed tube at about 190° for eight hours. The product was extracted with water and then crystallized from alcohol and finally from ligroïn, when it melted at 112°. It forms bright

* Jour. Chem. Soc., 1880, 752.

yellow plates or flattened prisms. This compound is more readily formed, however, from the silver salt. A nitrogen determination in a product thus obtained gave:

	Calculated for $C_{11}H_{12}N_2O_5$.	Found.
N	11.11	10.77

When this compound is treated with cold sodium hydroxide, the ethyl group is removed, leaving the acetyl group unaffected; on the other hand, when it is warmed with sulphuric acid, in alcoholic solution, the acetyl group alone is removed.

4-Nitro-2-aminobenzoic Acid. — This was best obtained by warming the acetyl compound in alcohol with acids. It separates from alcohol in long, bright-red needles. On heating it begins to darken at 260°, and then melts with decomposition at 264°. A nitrogen determination gave:

	Calculated for $C_7H_6N_2O_4$.	Found.
N	15.38	15.29

The *ammonium salt* was formed when dry ammonia gas was passed into an ethereal solution of the acid. It dissolves readily in water.

	Calculated for $C_7H_9N_3O_4$.	Found.
NH_3	8.58	8.49

The *sodium salt* was obtained as a bright-red precipitate when one molecular proportion of sodium ethylate was added to the alcoholic solution of the acid. It is quite soluble in water and sparingly in alcohol.

The *silver salt* was obtained as a pink, gelatinous precipitate when the above sodium salt was dissolved in water and the requisite amount of silver nitrate was added. On warming to about 50° and stirring, it coagulates to a tan-colored powder. The yield corresponds to the calculated.

	Calculated for $C_7H_5N_2O_4Ag$.	Found.
Ag	37.37	37.30

On treating this salt, suspended in ether, with the calculated quantity of acetyl chloride, enough heat was liberated to cause the solution to boil. It was warmed until the odor of acetyl chloride disappeared, then filtered, and evaporated over potassium hydrate in a vacuum desiccator. The crystals that separated proved to be 4-nitro-2-acetaminobenzoic acid.

Methyl 4-Nitro-2-aminobenzoate, obtained by boiling the acid with methyl alcohol and sulphuric acid, melts at 157°. It is soluble in ligroïn and alcohol, and separates in dark, orange-colored clusters of needles.

	Calculated for $C_8H_8N_2O_4$.	Found.
N	14.28	14.15

Ethyl 4-Nitro-2-aminobenzoate was obtained by boiling the acid with alcohol and hydrogen chloride. It forms dark, orange-colored plates, which are quite soluble in alcohol and benzene.

	Calculated for $C_9H_{10}N_2O_4$.	Found.
N	13.33	13.38

4-Nitro-2-ethylaminobenzoic Acid. — This was the chief product formed when the silver salt of the amino acid was suspended in ether and warmed with the calculated quantity of ethyl iodide for three days, the reaction then being practically complete. The ethereal solution was evaporated, and the residue treated with dilute sodium hydroxide; on filtering and acidifying the alkaline solution, this compound separated as a bright yellow precipitate. On crystallizing from alcohol and benzene it separated in the form of golden-yellow plates, which melt at about 223°. A nitrogen determination gave:

	Calculated for $C_9H_{10}N_2O_4$.	Found.
N	13.33	13.48

Ethyl 4-Nitro-2-ethylaminobenzoate. — The part insoluble after the above treatment with alkali proved to be this diethyl derivative. It is formed in smaller quantity than the nitrogen monoethyl derivative. From benzene and alcohol, in which it

is very soluble, it separates in the form of long, pale-yellow needles; these melt at 80°.

This compound was also formed when 4-nitro-2-ethylamino-benzoic acid was boiled with alcohol and sulphuric acid; an analysis therefore seemed superfluous.

Acetylorthoaminobenzoic acid was obtained when the silver salt of anthranilic acid was treated with acetyl chloride. It forms white prisms melting at 185°, as observed by Döbner and Miller.*

NEW HAVEN, January, 1898.

* Ber. d. chem. Ges., xv, 3077.

RESEARCHES ON THE CYCLOAMIDINES: PYRIMIDINE DERIVATIVES.*

By H. L. WHEELER.

For convenience of reference, in this work those compounds which have the amidine formation

I

$$RC\begin{matrix}\diagup\!\!\diagup NR'' \\ \diagdown NXR'\end{matrix} \quad II,$$

III

in which two of the radicals R, R′, and R″ are replaced by a ring structure or a bivalent grouping, are referred to as cycloamidines. The dotted lines in the above formula show the three possible ways of replacing the radicals, and they indicate three forms of cycloamidines. It will be noticed, however, that III is the tautomeric form of I. The tautomeric form of II is obtained when the position of the hydrogen X is changed to the opposite nitrogen atom. There are therefore only two types of cycloamidines, each type having a pseudomeric or tautomeric form, as in the case of the simple amidines.

The *first type*, which contains only one of the nitrogen atoms in the ring, is represented by such compounds as *a*-aminoquinoline, the *a*-aminobenzoxazines, etc.

The *second type*, with both nitrogen atoms in the ring structure, is found in the anhydro bases, glyoxalines, lophin, etc.

Then, further, combinations of these types and their tautomeric forms occur: The cyanalkines, *a*-amino- and anilidopyrimidines, aminoquinoxalines, cyanuramide, dicyanorthophenylenediamines, and the like, are examples of the combination types.

* Amer. Chem. Jour., xx, No. 6.

The object of the work, of which this paper gives a preliminary account, is primarily to investigate the action of alkyl halides on some of these cycloamidines which have not yet been examined in this respect, and also to compare this action in general with that of the simple amidines.

Pechmann* assumes that when a simple amidine, represented by the general formula above, is acted on with alkyl iodides, the hydrogen X is directly replaced, and hence this reaction serves to determine structure.

It seems to the writer that alkyl iodides may be added either to the amido group or to the imido group, or, when the substituents are similar,† to both and perhaps to the atoms joined by double union. In two of the latter cases an amidine would result of a different structure from that obtained by direct substitution, so that this method of determining structure seems to be not without objection.

The cycloamidines, in general, unite with alkyl iodides, and a number of cases have been described among those of the first type, where no direct substitution or replacement of hydrogen in the amino group takes place, at least not as the first step of the reaction. To illustrate this the following may be cited: Thiele and Ingle‡ obtained dialkylaminotetrazols by the action of alkyl iodides on aminotetrazol. They believe that in these only one of the alkyl groups replaces hydrogen of the amino group. Claus § shows that *a*-aminoquinoline takes up alkyl iodides in the same manner as the quinoline and pyridine bases in general, and that the amino-hydrogen is not substituted. Again, E. v. Meyer ‖ has shown in several cases that the cyanalkines form similar addition-products, the amino group not being substituted.

Even acyl chlorides add to the cyanalkines without substi-

* Ber. d. chem. Ges., xxviii, 2362 and 869.

† Pechmann (loc. cit.) found that when the substituents are similar radicals, the amidine gave two isomeric alkylated products. This is precisely what would be expected if the action is one of addition, there being in that case no decided tendency to addition entirely to either one of the nitrogen atoms.

‡ Ann. Chem. (Liebig), cclxxxvii, 249.

§ J. prakt. Chem., xvii, 209.

‖ Ibid., xxii, 266, and xxxix, 265.

tuting the amino group. Herfeldt* found that cyanbenzylin or aminophenyldibenzylmiazin unites with acetyl and benzoyl chlorides to form well-crystallized addition-products, and that an acetyl or benzoylcyanbenzylin was not obtained. In these cases it is a tertiary nitrogen which is the point of attack or addition.

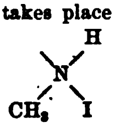
The action of alkyl iodides on the cycloamides of the second type is that of addition also, and, as in the case of the simple amidines, this action has generally been considered to be a direct replacement of hydrogen, since by treating the addition-product with alkali alkyl compounds result. The same question arises here as in the case of the simple amidines. That the alkyl group invariably replaces the hydrogen, however, has not been proved. It is not improbable that, like the cycloamidines of the first class, it is the tertiary nitrogen that unites with the alkyl halide.

The writer has found that phenylmethylanilidopyrimidine acts with methyl and ethyl iodides, forming stable addition-products, and that no substitution takes place. That the alkyl iodide unites with one of the tertiary nitrogen atoms of the ring, and not with the anilido group, follows in all probability from the behavior of these products with alkali:

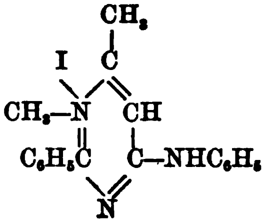
$$C_{17}H_{15}N_3.CH_3I + NaOH = C_{17}H_{15}N_3 + CH_3OH + NaI.$$

That is, methyl alcohol and sodium iodide are quantitatively formed, and unaltered anilidopyrimidine is regenerated. The formula that appears most probable for these addition-products is therefore either I or II, and from analogy a similar structure might be expected in the case of the alkyl halogen addition-products of the simple amidines.†

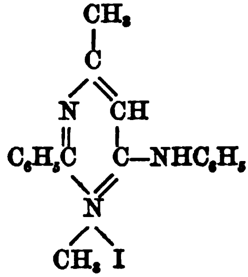
* J. prakt. Chem. [2], liii. 249.

† The fact that the alkyl iodide addition-products of the simple amidines give up hydrogen iodide and not the alkyl group as above cannot be considered as showing that the addition takes place to the –NH– group of the amidine. To be sure, the grouping  would be expected to give up

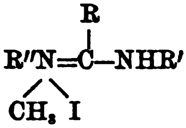
I.



II.



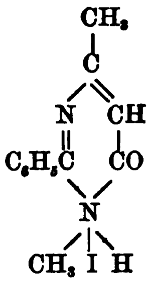
III.



This being the case, the structure of the simple amidines must be completely revised, and the opposite or so-called tautomeric structure must be assigned to them. At any rate, no method has yet been devised for determining the structure of the amidines in question that is without objection.

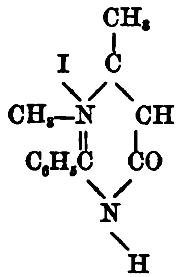
It will be shown below that phenylmethylpyrimidon, a cycloamidine of the second type, unites with one molecule of methyl iodide to form a beautiful crystalline addition-product of formula IV or V.

IV.



or

V.



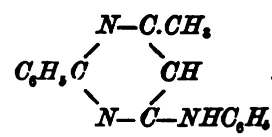
hydrogen iodide, and those alkyl iodide addition-products of the cyloamidines which do not separate hydrogen iodide most probably do not have this grouping. But it cannot be maintained that because an addition-product gives up hydrogen iodide, it has this grouping.

This compound, on treatment with alkali, gives up hydrogen iodide and not the alkyl group, and an alkylated pyrimidon results. This alkyl derivative differs decidedly from the product obtained by heating phenylmethylchlorpyrimidine with sodium methylate. The alkyl iodide therefore is added to one of the nitrogen atoms of the pyrimidon ring, while Pinner* found that, if the oxypyrimidine is heated with ethyl iodide in the presence of alkali, the ethyl group attaches itself to oxygen.

In order to determine to which nitrogen the alkyl halide is added, a synthesis of the methylpyrimidon was attempted as follows: Methylbenzamidine hydrochloride was prepared. This, with acetoacetic ester, according to Pinner's explanation of the formation of the pyrimidines, might be expected to give the base corresponding to formula IV. It was found, however, that methylbenzamidine does not give a pyrimidine derivative with acetoacetic ester, at least not under the same conditions that benzamidine does, so that for the present the question of the position of the alkyl group must be left undecided.

Nef† has shown that carbostyril is not acted on by ethyl iodide. The above pyrimidon differs from carbostyril, in its ring structure, in having a tertiary nitrogen. It would seem most probable, therefore, that it is due to this that the substance takes up methyl iodide, and that the addition-product is perhaps best represented by formula V.

Experimental Part.

Phenylmethylanilidopyrimidine,  .—
This was prepared according to Pinner's‡ directions by warming phenylmethylchlorpyrimidine with aniline. Instead of

* Die Imidoäther und ihre Derivate, 343.
† Ann. Chem. (Liebig), cclxxvi, 242.
‡ Die Imidoäther und ihre Derivate, 248.

purifying the material by dissolving the reaction-product in alcohol and precipitating it with ether, it was found best to crystallize it directly from water, precipitate the base from the hot aqueous solution, and then crystallize this from benzene and alcohol. The material thus obtained crystallizes in clusters of small prisms and melts at 160°–161°. Pinner gives its melting-point as 150°–153°.

The *hydrochloride* was obtained in colorless needles melting at 240°, as described by Pinner.

The *hydrobromide* was obtained by precipitating the base from a benzene solution with hydrobromic acid gas. It forms minute needles when crystallized from alcohol, and it melts at 250°.

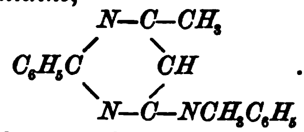
The *hydroiodide* forms colorless needles melting at 231°.

Phenylmethylanilidopyrimidine Methyl Iodide. — 6 g. of the above cycloamidine were heated with an excess of methyl iodide in methyl alcohol solution for seven hours from 100° to 105°. The material was then washed with alcohol and crystallized from water and alcohol. Thus obtained, the substance melts at about 210°–213° with strong effervescence. If suddenly heated, it melts much lower. The material dried in the air contains 2 molecules of water of crystallization (analyses I and II). When dried at a temperature of 130° it was obtained anhydrous (analysis III). Determinations I and III were made by dissolving the substance in water and precipitating with silver nitrate. Determination II was made by the method of Carius.

	Calculated for		Found.		
	$C_{18}H_{18}N_3I.2H_2O.$	$C_{18}H_{18}N_3I.$	I.	II.	III.
I . .	28.9	31.5	28.8	28.7	31.5

This addition-product is readily soluble in warm water and in alcohol, from which it crystallizes in fine, colorless needles. Ammonia or alkali immediately precipitates a substance melting at 160°–161°, which has all the properties of phenylmethylanilidopyrimidine.

Phenylmethylmethylanilidopyrimidine,



.— This was prepared by warming phenylmethylchlorpyrimidine with methyl aniline. It is the compound that should result by treating the above addition-product with alkali, if the action of methyl iodide on the cycloamidine takes place by substitution. A comparison of the above with the following properties shows that these compounds are different. This compound crystallizes from alcohol in colorless prisms which melt at 113°. It dissolves readily in ether, alcohol, and benzene, but is insoluble in water. A nitrogen determination gave:

	Calculated for $C_{18}H_{17}N_3$.	Found.
N	15.2	15.0

This compound dissolves readily in dilute hydrochloric acid, and platinum chloride gives a bright yellow, granular precipitate, which melts at about 228°, with effervescence.

The *hydroiodide* is readily soluble in warm alcohol, less readily in water. It melts, when slowly heated, at about 198°. An iodine determination gave:

	Calculated for $C_{18}H_{18}N_3I.2H_2O$.	Found.
I	28.9	28.9

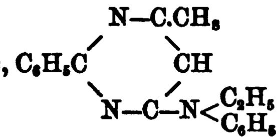
The *nitrate* separates from dilute nitric acid in long, colorless needles or prisms, which melt with violent effervescence at about 170°.

Phenylmethylanilidopyrimidine Ethyl Iodide.—This was obtained when 5 g. of phenylmethylanilidopyrimidine were heated with 10 g. of ethyl iodide for twelve hours at 120°–130°. The reaction-product was extracted with hot water, and then crystallized from alcohol, when it separated in colorless needles melting at about 215°. When crystallized from water the material shrivels at about 115°, then melts with effervescence at or near 215°. An iodine determination

in air-dried material indicates that the substance separates with one molecule of water of crystallization (analysis I). The material dried at 120°–130° becomes anhydrous (analysis II).

	Calculated for $C_{19}H_{20}N_3I.H_2O$.	Calculated for $C_{19}H_{20}N_3I$.	Found. I.	Found. II.
I	29.19	30.4	29.24	30.3

This addition-product and the analogous methyl compound give off the methyl iodides when heated to their melting-points. Ammonia or alkali precipitate phenylmethylanilidopyrimidine from aqueous or alcoholic solutions.

Phenylmethylethylanilidopyrimidine, 

— This was prepared like the corresponding methylanilidopyrimidine for the sake of comparison with the base obtained from the above addition-product. It is an entirely different base which melts at 87° when crystallized from alcohol. It is readily soluble in hot alcohol, difficultly in cold, and insoluble in water. It separates in beautiful, long, colorless prisms. A nitrogen determination gave:

	Calculated for $C_{19}H_{19}N_3$.	Found.
N	14.53	14.56

The *hydrochloride* is difficultly soluble in cold water, readily in hot, and crystallizes in colorless needles which appear to be hydrous. On heating, the material shrivels at about 100°, then melts at about 210°.

The *platinum chloride salt* separates as a bulky, light-yellow precipitate. It is insoluble in hot water, and melts at about 218°.

The *hydroiodide* crystallizes in prisms.

An attempt to prepare an ethyl bromide addition-product of phenylmethylanilidopyrimidine was unsuccessful. 3.8 g. of anilidopyrimidine were heated with an excess of ethyl bromide from 102° to 104° for five hours, when the material was

found to be unaltered. It was heated again, this time with the addition of some alcohol, the temperature being kept between 120° and 130° for seventeen hours. On opening the tube then, the products were found to be the hydrobromide of phenylmethylanilidopyrimidine described above, and ether. Ethyl bromide, therefore, neither effects substitution nor addition.

Phenylmethylpyrimidon Methyl Iodide. — Phenylmethyloxypyrimidine and methyl iodide, 4 g. of the former and 10 of the latter, were heated for six hours at 100°. No reaction was evident. The material was then heated for nine hours at 170°, when addition took place. The material dissolved almost entirely in water, and, on concentrating the aqueous solution to a syrup, a mass of needles was obtained. This was crystallized from alcohol, when beautiful, large, colorless prisms separated. These did not melt sharply, but decomposed with effervescence at 230°. An iodine determination gave:

	Calculated for $C_{11}H_{10}N_2O.CH_3I$	Found.
I	38.7	38.6

n-Methylphenylmethylpyrimidon. — When the above compound with methyl iodide was dissolved in a little water and dilute alkali was added, this compound separated as a mass of colorless needles. It was purified by crystallizing from water, when it separated in the form of beautiful, large prisms, which melt at about 91°–92°. A nitrogen determination gave:

	Calculated for $C_{12}H_{12}N_2O$	Found.
N	14.0	13.6

This compound has basic properties; it dissolves readily in dilute acids, the ordinary salts being all quite soluble. It is readily soluble in alcohol and ether, less readily in water, and is not dissolved by a small amount of alkali. The nitrate and platinum chloride double salt are the least soluble of the ordinary salts. These were obtained by spontaneous evaporation of the solutions.

The *nitrate* crystallizes in colorless, flattened prisms which melt with effervescence at about 195°.

The *platinum chloride* double salt separates in form of very large prisms with the color of azobenzene. It gave no definite melting-point below 275°, but turned dark at about 235°.

Methylbenzamidine hydrochloride, $C_6H_5C(NH)NHCH_3.HCl$. — This was prepared by dissolving benzimidoethylester hydrochloride in a 33 per cent solution of methylamine. On adding the hydrochloride to the solution of the amine the free ester separates; on shaking this dissolves, and in a short time a mass of colorless needles separates. This material was crystallized from water, in which it is not extremely soluble. A chlorine determination gave:

	Calculated for $C_8H_{10}N_2.HCl$.	Found.
Cl	20.82	20.75

The properties of this amidine hydrochloride apparently differ decidedly from those of the corresponding ethylamidine. Lossen * prepared ethylamidine hydrochloride in a state of purity only with some difficulty, while Pinner † obtained the hydroiodide as an oil which would not crystallize.

NEW HAVEN, March, 1898.

* Ann. Chem. (Liebig), cclxv, 159. † Ber. d. chem. Ges., xi, 7.

RESEARCHES ON THE CYCLO AMIDES: α-KETOBENZMORPHOLINE AND α-BENZPARAOXAZINE DERIVATIVES.*

By H. L. WHEELER and BAYARD BARNES.

α-KETOBENZMORPHOLINE, or from its method of preparation called orthoaminophenoxyacetic acid anhydride, has the structure of a cyclo amide and should act like an acid amide, or, in other words, as if it were a derivative of the two forms, $\overline{\text{NH—CO}}$ and $\overline{\text{N=COH}}$. The literature on this compound would seem to indicate that it is a very inactive substance, since no derivatives of it have hitherto been prepared. It will be shown, however, in this paper, that this compound behaves like an amide, and yields derivatives which, in their properties, are closely related to the corresponding compounds of formanilide.

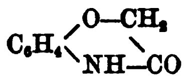
Orthoaminophenoxyacetic anhydride was first obtained by Fritzsche † by reducing orthonitrophenoxyacetic acid with stannous chloride. According to Thate, ‡ this compound is not obtained pure by Fritzsche's method, but is best prepared by reducing the nitro compound with iron and acetic acid.

Aschan § obtained this so-called anhydride from orthoaminophenol and chloracetyl chloride. He states that concentrated acids and alkalies have no effect on the substance, but that it reacts energetically with phosphorus pentachloride, with at least partial decomposition.

The latest work on the subject is that of Duparc. ‖ At Gräbe's suggestion he undertook the examination of this anhydride in order to determine which of the following formulas is to be assigned to the substance:

* Am. Chem. Jour., xx, No. 7.
† J. prakt. Chem. [2], xx, 288.
‡ Ibid. [2], xxix, 180.
§ Ber. d. chem. Ges., xx, 1523.
‖ Ibid., xx, 1943.

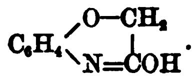
I.



(a-Ketobenzmorpholine.)

or

II.

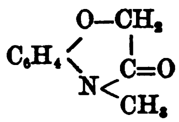


(a-Oxybenzparaoxazine.)

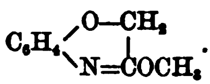
Duparc found that the material was not acted on by acetic anhydride even at 180°, and since he did not succeed in obtaining a reaction with methyl iodide or nitrous acid, he abandoned the subject.

We have taken up the work at this point, and find that a sodium and silver salt of this cyclo amide can easily be prepared, and that the action of alkyl iodides on these salts give two series of isomeric alkyl compounds. Those obtained from the sodium salt have the alkyl group joined to nitrogen, and are to be considered as α-ketobenzmorpholine derivatives (formula III), while those from the silver compound have the alkyl group attached to oxygen, and are cycloimido-esters or benzparaoxazine * derivatives (formula IV).

III.



IV.



The structure of these compounds is settled from the following: The product obtained by the action of methyl iodide on the sodium salt gave on prolonged heating with concentrated hydrochloric acid, at a high temperature, orthomethylaminophenol, $C_6H_4<^{OH}_{NHCH_3}$, thus showing, in the case of the sodium salts, that the alkyl groups attach themselves to nitrogen.

* Hitherto only two benzparaoxazine derivatives have been prepared. The compound obtained by reducing orthonitrophenylacyl ether, *i. e.*, $C_6H_4<^{O-CH_2}_{N=C.C_6H_5}$, and the analogous methyl derivative, are sometimes called β-phenyl and β-methylbenzparaoxazines (Ber. d. chem. Ges., xxiii, 172). From analogy with the quinoline derivatives, quinaldine, for example, being called α-methylquinoline, these compounds should be termed α- and not β-derivatives. The latter nomenclature is used in this paper.

On the other hand, the products obtained from the silver salt, even on treating with cold dilute hydrochloric acid, immediately regenerate *a*-ketobenzmorpholine. This instability in the presence of acids, being a characteristic property of substituted imido-esters, shows that in this case the alkyl groups are attached to oxygen.

It will be noticed that the above behavior of the sodium and silver salts of *a*-ketobenzmorpholine is perfectly analogous to that of the salts of the anilides. Indeed, the analogy by no means ends in this behavior, but extends also to the derivatives. The cycloimido-esters obtained from the silver salt of *a*-ketobenzmorpholine have strong, peculiar odors, and decompose into ketobenzmorpholine on exposure to the air; the isomeric compounds have no odor and are stable on exposure. The compounds from the silver salt behave precisely like the isoanilides or substituted imido-esters, not only in being immediately decomposed by acids, but also inasmuch as they react with bases, at ordinary temperature, giving amidines. These amidines, some of them difficult to crystallize, give well-crystallized salts.

Again, the silver salt of *a*-ketobenzmorpholine reacts with acyl chlorides, like the silver salts of the anilides, giving well-crystallized acyl derivatives. These derivatives have the acyl group attached to nitrogen. It is noteworthy that, in spite of the failure of Duparc to obtain an acetyl derivative by means of the keto compound and acetic anhydride, such a compound results, with evolution of heat, from the silver salt. Moreover, this acetyl compound is so stable that it can be crystallized from water without decomposition.

It is now shown that *a*-ketobenzmorpholine behaves precisely like formanilide, and therefore the normal structure is to be assigned to this cyclo amide (*i. e.*, formula I).

That the amides in general are derivatives of the structure $-\mathrm{NH}-\overset{|}{\mathrm{C}}\mathrm{O}$ and not $-\mathrm{N}{=}\overset{|}{\mathrm{C}}\mathrm{OH}$, or, in other words, that they have the keto and not the enol form, follows from the behavior of their oxy compounds.

It is well known that the oxy acids, especially the γ and δ derivatives, readily separate water, giving lactones. If the amides had the second of the above structures, they would be imido acids and their oxy compounds would be expected to separate water, like the oxy acids themselves, giving imidolactones; *viz.*,

$$HOCH_2CH_2CH_2C\begin{matrix}=NH \\ \diagdown OH\end{matrix} \rightarrow \underbrace{CH_2CH_2CH_2C}_{O}=NH.$$

Imidolactones have not yet been obtained. The oxyamides do not form anhydrides in this manner. For example: γ-oxyvaleramide results by heating γ-oxyvalerianic anhydride or the ester with ammonia to 100°. On boiling this oxyamide it slowly decomposes, giving off ammonia and not water; indeed some of these oxyamides boil unaltered. These facts not only show that the acid amides have the normal structure, but they also dispose of the theory that in these compounds the enol and keto form exist in a state of equilibrium.

Lachmann,* in his interesting paper on the constitution of the acid amides, concludes that acetamide and benzamide have hydroxyl groups because they *immediately* give off hydrogen chloride with phosphorus pentachloride. Oxamethane does not immediately decompose in this manner, but gives an amide chloride.† He therefore concludes that oxamethane has a keto group, and that these results point to a division of the amides into two groups, etc. The following considerations show, however, that this is not the true explanation of the behavior of these amides with phosphorus pentachloride. We know from the work of Wallach,‡ Lengfeld and Stieglitz,§ and others, that the grouping V (below) is very unstable, the grouping VI being more stable. It has been shown in papers from this laboratory that the more negative the character of the molecule in this or the analogous grouping VII, the less

* Amer. Chem. Jour., xviii, 600.

† Wallach, Ann. Chem. (Liebig), clxxxiv, 1.

‡ Ibid., clxxxiv, 1; ccxiv, 193.

§ Amer. Chem. Jour., xvii, 99.

stable are the compounds. What applies to grouping VII would therefore apply in greater force to grouping V.

$$\text{V.}\quad RC\begin{matrix}\diagup NHR' \\ \diagdown\!\!\diagdown Cl_2\end{matrix}, \qquad \text{VI.}\quad RC\begin{matrix}\diagup\!\!\diagup NR' \\ \diagdown Cl\end{matrix}, \qquad \text{VII.}\quad RC\begin{matrix}\diagup\!\!\diagup NR' \\ \diagdown OC_2H_5\end{matrix}.$$

We now have the true explanation of Lachmann's results. The amide chlorides of acetamide and benzamide are far more negative than the amide chloride of carbonic acid or its ester-amide oxamethane, and, as would be expected, they decompose more easily. The different behavior of the amides with phosphorus pentachloride, therefore, does not depend on a difference of structure but on the properties of the amide chlorides.

If this view is correct, it must follow that if we increase the positive character of the molecule VI by replacing radical R by an imido or anilido group, for example, we should obtain a compound capable of forming a comparatively stable amide chloride corresponding to formula V. This is precisely what takes place. Lengfeld and Stieglitz,* in their interesting work on the imido-ethers of carbonic acid, have shown that carbodiphenylimide, $C_6H_5N{=}C{=}NC_6H_5$, not only unites with one molecule of hydrogen chloride, as stated by Weith, giving an imide chloride (formula VIII), but that this compound combines further with hydrogen chloride, and, as would be expected, a stable amide chloride results, which they call carbodiphenylimide dichloride (formula IX).

$$\text{VIII.}\quad C_6H_5NH{-}C\begin{matrix}\diagup\!\!\diagup NC_6H_5 \\ \diagdown Cl\end{matrix}, \qquad \text{IX.}\quad C_6H_5NH{-}C\begin{matrix}\diagup NHC_6H_5 \\ \diagdown\!\!\diagdown Cl_2\end{matrix}.$$

Lengfeld and Stieglitz state that this amide chloride melts at 130° and "is quite stable when kept from moisture and organic matter."

From the above it is evident that the results obtained by the action of phosphorus pentachloride on acet- and benz-

* Amer. Chem. Jour., xvii, 108.

amides do not lead to the conclusion that these compounds have a hydroxyl group. Indeed, it is very improbable that the grouping $-N{=}\overset{|}{C}OH$ exists in any stable amide whatever.

Experimental Part.

a-Ketobenzmorpholine, $C_6H_4\left\langle\begin{array}{l}O{-}CH_2\\NH{-}CO\end{array}\right\rangle$. — This was prepared essentially according to Thate's method.* His directions for the purification of both orthonitrophenyloxyacetic acid and the anhydride, obtained by reduction, not being suitable for the preparation of the material in large quantities, it was found better to proceed as follows:

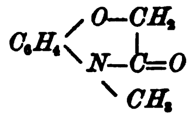
After warming the mixture of orthonitrophenol, chloracetic acid and alkali, and filtering, hydrochloric acid was added, and the precipitate distilled in steam to remove unaltered orthonitrophenol. The aqueous solution remaining deposits the orthonitrophenyloxyacetic acid on cooling. For the reduction the acid was suspended in about 20 per cent acetic acid and iron filings slowly added. After the reduction, the residue was boiled with alcohol and animal charcoal and the anhydride crystallized from alcohol. The melting-point of the material thus obtained is 169°, instead of 166° as given by Thate. It may be crystallized conveniently from alcohol or chloroform. In the latter solvent it is less soluble.

a-Sodiumoxybenzparaoxazine, $C_6H_4\left\langle\begin{array}{l}O{-}CH_2\\N{=}\overset{|}{C}ONa\end{array}\right.$. — 0.8 g. of sodium was dissolved in methyl alcohol, and 5 g. of *a*-ketobenzmorpholine were added. The solution was then evaporated in a vacuum, and the residue heated at 100° for several hours, the pressure being kept at about 13 mm. The perfectly dry mass then, on shaking, became granular, and a sodium determination as carbonate gave:

	Calculated for $C_8H_7NO_2.CH_3.ONa$.	Calculated for $C_8H_6NO_2Na$.	Found.
Na . . .	11.33	13.45	13.41

* J. prakt. Chem. [2], xxix, 148.

The material thus obtained did not dissolve in water, but α-ketobenzmorpholine separated; on adding an excess of alkali this readily dissolved. An attempt to prepare this sodium salt by dissolving the keto compound in alcohol, adding the calculated quantity of sodium ethylate, and then ether, gave no precipitate.

n-Methyl-α-ketobenzmorpholine,  . — This compound was prepared by heating the dry sodium salt of α-ketobenzmorpholine, suspended in benzene, to 135° for several hours. It was found, however, that it is unnecessary to prepare the dry salt as given above. It was more conveniently prepared as follows: 1.6 g. of sodium were dissolved in a small amount of methyl alcohol, 10 g. of α-ketobenzmorpholine were added, and then 20 g. of methyl iodide; the whole was then heated to 135° for about seven hours. The contents of the tube were then filtered from sodium iodide, washed with ether, and distilled at 14 mm. pressure. After the alcohol and ether had evaporated, the material practically all boiled over at 156°. It readily solidified, and, on crystallizing from alcohol, large, stout, colorless prisms were obtained. These melted from 58° to 59°, and a nitrogen determination gave:

	Calculated for $C_9H_9NO_2$.	Found.
N	8.58	8.58

It was found that this compound, like the following ethyl derivative, has little or no basic properties. It is insoluble in cold dilute hydrochloric acid. On warming, solution takes place, but, on cooling, the unaltered material separates in the form of needles or prisms. It dissolves more readily in concentrated hydrochloric acid, and is precipitated by water. Platinum chloride gave no precipitate when added to these solutions. A solution of the material in benzene gave no precipitate with dry hydrogen chloride. It is insoluble in alkali.

Orthomethylaminophenol, $C_6H_4\begin{array}{l}\diagup OH\\ \diagdown NHCH_3\end{array}$. — Not quite 2 g. of the above methyl derivative were heated with concentrated hydrochloric acid to 150°–160° for a number of hours. The hydrochloric acid was then evaporated on the water-bath and the residue treated with water, when it was found that the greater portion of the material had remained unaltered in this treatment; the aqueous filtrate was treated with an excess of sodium carbonate, some sulphurous acid was added, and the whole shaken with ether. On evaporating the ether solution a small amount of almost colorless material separated in the form of plates. This was crystallized from petroleum ether, when colorless, thin spangles separated. On heating the pure material thus obtained, it began to darken in color rapidly at 80°, and decomposed, melting and turning black between 80° and 90°. Seidel,* who first obtained this compound, states that it crystallizes in plates that soon oxidize and take on a dark brown color. He says that, on heating, the material darkens and then melts above 80° with decomposition. The properties of the compound obtained by us agree perfectly with this description. We may add, as a further means of identifying this compound, that the hydrochloric acid solution gives a deep red-brown color with ferric chloride.

n-Ethyl-a-ketobenzmorpholine, $C_6H_4\begin{array}{l}\diagup OCH_2 \diagdown\\ \diagdown N(C_2H_5) \diagup\end{array}CO$. — This was prepared by means of sodium ethylate and ethyl iodide in the same manner as the above methyl derivative. The contents of the tube after the evaporation of the excess of ethyl iodide and alcohol all boiled over from 157° to 159° at 15 mm. pressure. This material, unlike the methyl compound, was not obtained in the solid state. It had a light yellow color, and a nitrogen determination gave:

	Calculated for $C_{10}H_{11}NO_2$.	Found.
N	7.91	8.20

* J. prakt. Chem., xlii, 453.

This compound, like the corresponding methyl derivative, is not affected by acids or alkali under ordinary conditions. It dissolves in concentrated hydrochloric acid, and is precipitated again by water. A slight warming is noticed on dissolving the material in concentrated sulphuric acid.

a-Silveroxybenzparaoxazine, $C_6H_4\left\langle\begin{array}{l}O{-}CH_2\\ \quad\;\; | \\ N{=}COAg\end{array}\right.$. — This was prepared by dissolving *a*-ketobenzmorpholine in alcohol and adding, first, sodium ethylate (1 molecule) and then the calculated quantity of silver nitrate. The mixture, largely diluted with water, gave a white precipitate which, on stirring, became a light gray powder. This was filtered, washed with water, alcohol, and ether, and dried at a temperature somewhat below 100°. A silver determination gave the following:

	Calculated for $C_8H_6NO_2Ag$.	Found.
Ag	42.18	42.37

This salt is quite stable in respect to light. It is not readily decomposed by water or alcohol, although phenol immediately reduces it. The behavior of the silver salts of this compound and formanilide with phenols, is peculiar. Silver formanilide and silver 2-4-dichlorformanilide react with phenol with evolution of heat, the salts immediately blackening and regenerating unaltered formyl compound and silver. This is all the more remarkable, since silver 2-4-dichlorformanilide may stand mixed with water or alcohol for days without decomposition. Indeed, it can be boiled with water without any decomposition. Cold glycerin does not affect it, but phenol, largely diluted with benzene, an aqueous solution of hydroquinone, or an alcoholic of β-naphthol, almost immediately reduces the salt. A solution of thymol in benzene produces a mirror of silver, and resorcin in water slowly blackens the compound. From the above it is evident that these reactions involve an addition; the addition-products being unstable then decompose into simpler molecules.

α-Methoxybenzparaoxazine, $C_6H_4\left\langle\begin{matrix}O-CH_2\\ \quad\;|\\ N=COCH_3\end{matrix}\right.$. — 20 g. of α-silver oxybenzparaoxazine and 20 g. of methyl iodide (1.5 molecules) were heated to 115°–120° for eight hours, the reaction then being practically complete. The material was then taken up in ether and filtered from the silver iodide.* The ether solution on evaporation in a vacuum over potash gave an oil which refused to solidify in a freezing-mixture. It was found to boil almost entirely between 135° and 136° at 21 mm. pressure. The material thus obtained was a colorless oil with a pleasant odor, perhaps suggesting orange peel. A nitrogen determination gave:

	Calculated for $C_9H_9O_2N$.	Found.
N	8.58	8.66

On treating this oil with a drop of dilute hydrochloric acid it immediately solidified, giving crystals of α-ketobenzmorpholine. On exposure to air it slowly absorbs moisture, giving the same result. It is unaffected by cold alkali.

α-Ethoxybenzparaoxazine, $C_6H_4\left\langle\begin{matrix}O-CH_2\\ \quad\;|\\ N=COC_2H_5\end{matrix}\right.$. — 23 g. of the above silver salt were heated with ethyl iodide (2 molecules) to 100°–130° for twenty hours. On extracting with ether and evaporating, an oil was obtained which deposited some unaltered α-ketobenzmorpholine. On distilling in a vacuum the oil boiled mostly between 135° and 136° at 16 mm. pressure. It had a similar pleasant odor to that of the methoxy compound. A nitrogen determination gave:

	Calculated for $C_{10}H_{11}O_2N$.	Found.
N	7.90	7.68

With acids this compound is immediately decomposed like the methoxy compound. It is unaffected by cold alkali.

* It is advisable to shake the ether solution with alkali in order to remove unaltered orthoaminophenoxyacetic acid anhydride, which always accompanies the reaction-product. Compare α-isoamyloxybenzparaoxazine.

α-Isopropyloxybenzparaoxazine, $C_6H_4\left\langle\begin{matrix} O-CH_2 \\ \quad\; | \\ N-COC_3H_7 \end{matrix}\right.$. — 25 g. of the silver salt and 22 g. of isopropyl iodide were heated for nine hours at 120°–130°. On extracting them with ether, shaking the ether solution with dilute potassium hydroxide, and evaporating, an oil was obtained. This was distilled at 14 mm. pressure, when the greater portion boiled from 137° to 138°. The material was colorless and had a peculiar odor, which, unlike the methyl and ethyl derivatives, was not pleasant. A nitrogen determination gave:

	Calculated for $C_{11}H_{13}O_2N$.	Found.
N	7.32	7.31

It decomposes on standing, or with acids, giving *α*-ketobenzmorpholine.

α-Isobutyloxybenzparaoxazine, $C_6H_4\left\langle\begin{matrix} O-CH_2 \\ \quad\; | \\ N=COC_4H_9 \end{matrix}\right.$. — 25 g. of the silver salt and 26 g. of isobutyliodide were heated for twenty-two hours at 120°–140°. The reaction-product, treated as above, gave an oil which was distilled at 21 mm. pressure, when it was found to boil practically from 160° to 164°. It had a strong, somewhat disagreeable odor. A nitrogen determination gave:

	Calculated for $C_{12}H_{15}O_2N$.	Found.
N	6.82	6.83

α-Isoamylbenzparaoxazine, $C_6H_4\left\langle\begin{matrix} O-CH_2 \\ \quad\; \diagdown \\ N=C-OC_5H_{11} \end{matrix}\right.$. — 25 g. of the silver salt and 28 g. of isoamyl iodide were heated to 130°–150° for eighteen hours. On extracting with ether, an oil was obtained which gave no constant boiling-point, the solid anhydride distilling over with the oil. The distillate was taken up in ether and shaken with dilute potassium hydrate; the ether was evaporated and the oil then distilled at 174°–175° at 21 mm. pressure. It was colorless and had

a disagreeable odor, somewhat resembling isoamyl oxalate. A nitrogen determination gave:

	Calculated for $C_{12}H_{17}O_3N$.	Found.
N	6.39	6.55

n-Acetyl-a-ketobenzmorpholine, $C_6H_4\Big\langle\begin{array}{l} OCH_2 \\ N\ COCH_3 \end{array}\Big\rangle CO$. — Acetyl chloride reacts violently with dry *a*-silver oxybenzparaoxazine. For the preparation of this compound 6 g. of the silver salt were suspended in dry ether, and the calculated amount of acetyl chloride was added. On filtering and evaporating, beautiful, long, white needles separated; these melted at 77°. A nitrogen determination gave:

	Calculated for $C_{10}H_9O_3N$.	Found.
N	7.32	7.43

This acyl compound is quite stable. It can be crystallized unaltered from water.

n-Benzoyl-a-ketobenzmorpholine, $C_6H_4\Big\langle\begin{array}{l} O-CH_2 \\ N-COC_6H_5 \end{array}\Big\rangle CO$. — 6 g. of the silver salt were suspended in benzene and benzoyl chloride added. From the benzene solution beautiful, colorless, compact prisms separated. These melted at 93°, and a nitrogen determination gave:

	Calculated for $C_{15}H_{11}O_3N$.	Found.
N	5.53	5.46

This compound can be crystallized from water.

a-Phenylaminobenzparaoxazine, $C_6H_4\Big\langle\begin{array}{l} O-CH_2 \\ \quad\quad\ \ | \\ N=C-NHC_6H_5 \end{array}$. — When *a*-ethoxybenzparaoxazine and aniline were mixed, in molecular proportions, the mixture solidified after standing twenty-four hours to a white, crystalline mass. It is readily soluble in alcohol, from which it crystallizes in colorless, compact prisms melting at 126°. A nitrogen determination was made with the following result:

	Calculated for $C_{14}H_{12}N_2O$.	Found.
N	12.50	12.53

The *hydrochloride* prepared by dissolving the above cycloamidine in aqueous hydrogen chloride separated in the form of colorless, four-sided prisms, which melt with decomposition from 220° to 223°.

The *hydroiodide*, $C_{14}H_{12}N_2O.HI$, crystallizes from water in colorless plates, which melt from 195° to 196°. An iodine determination gave:

	Calculated for $C_{14}H_{13}N_2OI$.	Found.
I.	36.26	35.77

The *nitrate* separates from dilute nitric acid in the form of colorless four- and eight-sided plates, melting at 147°.

a-Metachlorphenylaminobenzparaoxazine,

$$C_6H_4\left\langle\begin{array}{l} O-CH_2 \\ \quad\quad | \\ N=C-NC_6H_4Cl \end{array}\right. .—$$

A mixture of *a*-ethoxybenzparaoxazine and one molecular proportion of metachloraniline did not solidify after standing a week. The material was then taken up in dilute hydrochloric acid, and, after filtering, the amidine was precipitated with ammonia. It was then obtained in the solid condition, and, on crystallizing from benzene, it separated in the form of colorless plates, and melted at 112°–114°.

	Calculated for $C_{14}H_{11}N_2O.Cl$.	Found.
N	10.83	10.06

The *hydrochloride*, $C_{14}H_{10}N_2OCl.HCl$, crystallized from alcohol, melts with decomposition at 205°–207°.

a, β-Naphthylaminobenzparaoxazine,

$$C_6H_4\left\langle\begin{array}{l} O-CH_2 \\ \quad\quad | \\ N=C-NHC_{10}H_7 \end{array}\right. .—$$

2.4 g. of *a*-isopropylbenzparaoxazine and 2 g. of *β*-naphthylamine were heated in alcohol for eighteen hours on the steam-bath. On evaporating off the alcohol and crystallizing the

residue from benzene, white leaflets separated which melted from 154° to 155°.

	Calculated for $C_{12}H_{14}N_2O$.	Found.
N	10.22	10.00

a-Isobutylaminobenzparaoxazine, $C_6H_4\left\langle\begin{array}{l}O-CH_2\\ \quad\ \ \vert\\ N=C-NHC_4H_9\end{array}\right.$.—This was obtained by mixing *a*-ethoxybenzparaoxazine with isobutylamine. It forms a thick varnish at ordinary temperature, which, only after long standing, showed evidence of crystallization.

The *hydrochloride* may be crystallized from water or chloroform. From the latter it separates in the form of flakes, melting from 220° to 223°.

	Calculated for $C_{12}H_{17}N_2OCl$.	Found.
Cl	14.76	14.40

a-Allylaminobenzparaoxazine, $C_6H_4\left\langle\begin{array}{l}O-CH_2\\ \quad\ \ \vert\\ N=C-NHC_3H_5\end{array}\right.$.—The mixture in this case did not solidify on long standing. It was taken up in benzene and the hydrochloride precipitated by means of dry hydrogen chloride. This precipitate was crystallized from benzene containing some alcohol, when colorless needles, melting at 190°, were obtained. These were dissolved in alcohol. From the solution, ammonia precipitated an oil which soon solidified. This was crystallized from ligroïn with a little benzene, when the material separated in colorless prisms melting at 63°.

The *hydrochloride* is readily soluble in water and alcohol; it was analyzed with the following result:

	Calculated for $C_{11}H_{13}N_2OCl$.	Found.
Cl	15.8	15.9

NEW HAVEN, May, 1898.

THE ACTION OF AMINES ON ACYL IMIDO-ESTERS: ACYLAMIDINES.*

BY H. L. WHEELER AND P. T. WALDEN.

IN a previous paper we described a series of acyl imido-esters, and stated that they react with ammonia and bases giving acylamidines. We are now prepared to describe some of these amidines and to discuss their formation.

Few acylamidines have hitherto been described. The action of acyl chlorides and anhydrides on the free amidines does not always lead to the formation of acyl derivatives.* Pinner obtained benzoylbenzamidine from benzamidine and benzoic acid anhydride, and also from benzonitrile by condensation with sulphuric acid. On account of the ease with which this compound separates ammonia, giving dibenzamide, he assigned the structure represented by formula I to this substance.

We have found that the benzoylbenzimido esters, *i. e.*,

$$C_6HC_5C\begin{array}{l} /\!\!/ NCOC_6H_5 \\ \diagdown OR \end{array}$$

react with ammonia, giving a compound in every respect identical with that obtained from benzonitrile by the method of Pinner, while an isomeric compound (formula II) would be expected, if the reaction takes place, as is usually assumed, by double decomposition, replacement, or substitution.

$$\begin{array}{cc} \text{I.} & \text{II.} \\ C_6H_5C\begin{array}{l} / NHCOC_6H_5 \\ \diagdown\!\!\diagdown NH \end{array} & C_6H_5C\begin{array}{l} /\!\!/ NCOC_6H_5 \\ \diagdown NH_2 \end{array} \end{array}$$

The action of amines on the acyl imido-esters, like the action of amines on the amidines themselves, does not take

* Amer. Chem. Jour., xx, No. 7.

† Pinner, Die Imidoäther und ihre Derivate.

place by direct replacement, but involves the intermediate formation of an unstable addition-product:

III.

$$C_6H_5C\begin{array}{l}\diagup\!\!\diagup NCOR \\ \diagdown OR\end{array} + H_2NH = C_6H_5C\begin{array}{l}\diagup NHCOR \\ -OR \\ \diagdown NH_2\end{array}$$

This hypothetical addition-product can then separate alcohol in two ways, giving an acylamidine corresponding to either of the above forms.

It cannot be maintained that, because benzoylbenzamidine easily decomposes into dibenzamide and ammonia, its structure is to be represented by formula I, since in this decomposition hydrolysis takes place with addition of water, forming a product similar to III, and the same addition-product must result from I and II.

That this view is correct, and that this decomposition has no significance in regard to the structure of the acylamidines, is shown by the behavior of the analogously constituted acyl imido-esters, *i. e.*, benzoylbenzimidoethyl ester and benzoylphenylacetimidoethyl ester. These compounds easily decompose with water, under the same conditions as benzoyl, benzamidine, as follows:

$$C_6H_5C\begin{array}{l}\diagup\!\!\diagup NCOC_6H_5 \\ \diagdown OC_2H_5\end{array} \rightarrow C_6H_5C\begin{array}{l}\diagup NHCOC_6H_5 \\ -OH \\ \diagdown OC_2H_5\end{array}$$

$$C_6H_5CH_2C\begin{array}{l}\diagup\!\!\diagup NCOC_6H_5 \\ \diagdown OC_2H_5\end{array} \rightarrow C_6H_5CH_2C\begin{array}{l}\diagup NHCOC_6H_5 \\ -OH \\ \diagdown OC_2H_5\end{array}$$

That is, the first gives dibenzamide and alcohol, while the second gives benzamide and ethylphenyl acetate. In other words, the first apparently decomposes at a single bond; the second at the double bond. Here are then two compounds, not only of the same structure, but also similar to the acyl-

amidines, which decompose or are hydrolyzed in two different ways.

The structure of these amidines cannot therefore be determined by their decomposition-products, and further work will be required before this question is settled.

Beckmann and Sandal,* in their interesting work on the rearrangement of α-benzilmonoxime, have recently obtained benzoylbenzimidochloride, $C_6H_5C\begin{smallmatrix}\nearrow NCOC_6H_5\\ \searrow Cl\end{smallmatrix}$, a compound which shows, as would be expected, many properties in common with the acylimido esters. It readily decomposes into dibenzamide, and unites with primary bases giving acyl amidines. With ammonia it gives the acyl amidine described by Pinner, and with aniline and acyl amidine identical with that obtained by us from the benzoylbenzimido esters. Beckmann and Sandal, however, did not succeed in preparing acyl amidines from this compound and secondary amines, and here it may be stated that we have repeatedly made attempts to prepare acyl amidines from secondary bases and various acylimido esters, but in each case also without success.

In support of Pinner's formula for benzoylbenzamidine, Beckmann and Sandal state that benzaldehyde does not combine with this substance, and that with benzenesulphochloride it gives a compound insoluble in alkali.

The acyl amidines, described below, are stable towards cold alkali. Some of them dissolve in acids and may be precipitated unaltered by alkali or ammonia. They combine with one equivalent of hydrogen chloride to form salts which are comparatively unstable. In aqueous solution these salts soon decompose as follows:

$$C_6H_5C\begin{matrix} NHCOR \\ \diagup \\ —Cl \\ \diagdown \\ NHC_6H_5 \end{matrix} + H_2O = \begin{matrix} C_6H_5CO.NHCO.R \\ + \\ C_6H_5NH_2.HCl \end{matrix}$$

The diacylamide generally separates pure and in the form of a glistening mass of colorless crystals.

* Ann. Chem. (Liebig), ccxcvi, 279.

Experimental Part.

Benzoylbenzamidine. — This was formed when 10 g. of benzoylbenzimidonormalpropyl ester were warmed in alcoholic solution with the addition of aqueous ammonia in excess. On diluting the alcoholic solution, in which it is readily soluble, this compound separated as an oil which readily solidifies. It was purified by dissolving or crystallizing it from a mixture of ligroïn and alcohol. It melted constantly at 100°. Pinner * gives the melting-point of this compound as 106°. Gumpert † states that it melts at 105.5°, and Beckmann and Sandal give 98° as its melting-point. In addition to the above we have prepared this compound from benzoylbenzimidoethyl ester and ammonia. This product also melted at 100°. A nitrogen determination in the sample prepared as first stated gave:

	Calculated for $C_{14}H_{12}N_2O$.	Found.
N	12.50	12.53

In order to determine whether this compound is identical with that obtained by Pinner, we have prepared the substance by dissolving benzonitrile in fuming sulphuric acid, according to his directions, and have found that the compound thus obtained also melted sharply at 100° to 101°. A crystallographic examination of the two products was made by Mr. C. H. Warren, to whom the authors wish to express their thanks for the following report: "A trial on the reflection goniometer showed that the faces gave poor reflections, consisting of a number of faint signals for each face, and that a full description was not practicable. However, enough measurements were made of the same zone on both lots of crystals to show satisfactorily the identity of the two specimens. The crystals show monoclinic symmetry. The forms observed were *c* 101 (?), *y* $10\bar{1}$ (?), and *m* 110, probably. On many of the crystals the edges between the prism and top faces were highly modified. The measurements of zone $c \wedge y$ were as follows:

* Loc. cit.

† J. prakt. Chem., xxx, 90.

	Ours.	Pinner's.
$c \wedge y$	49° 9′	49° 10′
$y \wedge c'$	130° 51′	130° 40′

The angles measured agree closely considering the poor quality of the reflections." The crystallographic and chemical properties therefore show that the two products are identical. On warming the hydrochloric acid solutions, both products give dibenzamide.

Benzoylbenzamidine Hydrochloride, $C_6H_5C{\begin{matrix} \diagup NHCOC_6H_5 \\ -Cl \\ \diagdown NH_2 \end{matrix}}$.—

The above amidine was dissolved in benzene containing some chloroform, and the solution was saturated with hydrogen chloride, when a heavy, thick oil separated. This oil consists probably of a dihydrochloride. It is very unstable. The material was protected from moisture, and dry carbon dioxide was led in, to expel the excess of hydrogen chloride. After a number of hours the material crystallized in small colorless prisms. On pressing on paper it was found to be somewhat sticky. It was then heated to 50°, when considerable hydrogen chloride escaped, and the mass became a sandy powder. Thus obtained, it melted, not sharply, at about 190°, and a chlorine determination gave the following:

	Calculated for $C_{14}H_{12}N_2O.Cl$.	Found.
Cl	13.6	12.9

This salt is readily soluble in water, and decomposes with the separation of dibenzamide.

The *platinum chloride double salt* was obtained by dissolving the amidine in aqueous hydrochloric acid and adding platinum chloride. It separates as a straw-yellow precipitate which darkens on heating at about 225° to 230°, and melts at 240°. A platinum determination gave:

	Calculated for $(C_{14}H_{12}N_2O.HCl)_2PtCl_4$.	Found.
Pt	22.7	22.5

Benzoylethylbenzamidine. — This was prepared by allowing 6 g. of benzoylbenzimidonormalpropyl ester to stand in alcohol for some time mixed with an excess of a 33 per cent solution of ethylamine. The alcohol was then evaporated, and it was attempted to crystallize the residue from dilute alcohol, ligroïn, and benzene, but a sharp melting-point was not obtained until the material was dissolved in dilute hydrochloric acid, precipitated by ammonia, and then crystallized from strong alcohol. Thus obtained, it separated in beautiful colorless prisms which melted at about 87° to 88°. This compound is undoubtedly identical with the compound obtained by Lossen* by acting on ethyl benzamidine with benzoyl chloride. He gives the melting-point as 88°.

Benzoylphenylbenzamidine. — 4 g. of benzoylbenzimidoethyl ester were mixed in ether with 1.5 g. of aniline. No evidence of any reaction was noticed after standing over night. The ether was then evaporated, and the residue heated on the steam-bath, when it solidified. The material was found to crystallize beautifully from alcohol, apparently in thick bunches of rhombohedra. The material is insoluble in cold dilute sodium hydrate and melts at 148°. This gave on analysis:

	Calculated for $C_{20}H_{16}N_2O$.	Found.
N	9.33	6.32

This compound has recently been obtained by Beckmann and Sandal.† They find that the compound melts at precisely the same temperature that we have observed.

When dry hydrogen chloride was passed into a chloroform solution of this acylamidine, no precipitate resulted. On evaporating the chloroform in a stream of dry carbon dioxide, an amber-yellow varnish remained. When warmed with water, this gave a mass of colorless needles or prisms, which melted at 149°, and had all the properties of dibenzamide.

An attempt was made to prepare *benzoylmethylphenylbenzamidine* by acting on benzoylbenzimidoethyl ester with mono-

*Ann. Chem. (Liebig), cclxv, 162.

† Loc. cit.

methylaniline, when it was found that this secondary aniline did not give an acyl amidine. 4 g. of the acyl imido-ester and 1.7 g. of methylaniline were heated to 100°, then for some time kept at about 70°, and finally, after long standing, crystals separated. These crystallized from alcohol in prisms melting at 147°–148°. A nitrogen determination gave:

	Calculated for Acylamidine.	Calculated for Dibenzamide.	Found.
N	8.91	6.22	6.17

With ethylaniline the same result was obtained. The above analyzed material was soluble in alkali and precipitated again by acids; it was therefore dibenzamide.

Acetylphenylbenzamidine. — When acetylbenzimidoethyl ester is mixed with aniline and allowed to stand, the mixture solidifies. On crystallizing from 95 per cent alcohol, it forms stout, colorless crystals, which melt at 138.5°. A nitrogen determination gave:

	Calculated for $C_{15}H_{14}N_2O$.	Found.
N	11.76	11.94

Acetylparatolylbenzamidine. — *p*-Toluidine and acetylbenzimidoethyl ester were mixed in molecular proportions and allowed to stand, when the mixture soon solidified. The material was crystallized from 50 per cent alcohol, when it was found to melt at 136.5°. A nitrogen determination gave:

	Calculated for $C_{16}H_{16}N_2O$.	Found. I.	Found. II.
N	11.11	11.30	11.30

Acetylmetachlorphenylbenzamidine. — 1.5 g. of acetylbenzimidoethyl ester and 1 g. of metachloraniline on mixing solidify after some time. The material crystallized from alcohol separates in clusters of colorless needles or prisms. It melts at 128°–129°. A nitrogen determination gave:

	Calculated for $C_{15}H_{13}N_2OCl$.	Found.
N	10.27	10.08

A portion of the analyzed material was dissolved in dry benzene, and the solution was saturated with hydrogen chloride, when a sticky precipitate separated. The excess of hydrogen chloride was expelled by means of a current of dry carbon dioxide. The precipitate, unsuitable for analysis, dissolved readily in water, and, on warming up to 80°, colorless needles separated. These melted from 118° to 119° (acetbenzamide), and dissolved readily in dilute sodium hydroxide. The solution on standing deposited plates (benzamide).

2,4-Xylylbenzamidine. — When 2,4-xylidine and acetylbenzimidoethyl ester were mixed and allowed to stand a long time, a solid separated. The material was too soluble to crystallize from alcohol. The alcoholic solution was precipitated with dilute potassium hydrate, in order to remove any acetbenzamide, when an oil separated. This, on standing, solidified to a mass of prisms. The material was readily soluble in warm ligroïn, and crystallized in long, colorless needles, melting at 106°. Nitrogen determinations showed that this is not the expected acetyl-2,4-xylylbenzamidine, but that the acetyl group had been removed.

	Calculated for Acylamidine $C_{17}H_{18}N_2O$.	Calculated for Amidine $C_{15}H_{16}N_2$.	Found. I.	Found. II.
N . . .	10.52	12.50	12.34	12.36

The material dissolved readily in dilute hydrochloric acid, and gives a yellow precipitate with platinum chloride.

Acetyl-β-naphthylbenzamidine was formed when β-naphthylamine was warmed with acetylbenzimidoethyl ester. The product was crystallized from 95 per cent alcohol, when it melted at 137°. A nitrogen determination gave:

	Calculated for $C_{19}H_{16}N_2O$.	Found.
N	9.72	9.64

Propionylphenylbenzamidine. — When propionylbenzimidoethyl ester was mixed with aniline, the mixture solidified in about four or five hours. It was crystallized from alcohol,

when small, stout prisms of a yellowish-white color were obtained. These melt at 138°, and a nitrogen determination gave:

	Calculated for $C_{16}H_{16}N_2O$.	Found.
N	11.11	11.01

Dry hydrogen chloride led into a benzene solution of this acylamidine gave a sticky precipitate. It was dissolved in water, and in a few minutes a mass of colorless prisms separated. These melted at 98°, and are propionylbenzamide, which compound we described in a previous paper. On warming this with aqueous ammonia, the material dissolved, and, on cooling, plates of benzamide separated, melting at 128°.

An attempt was made to prepare *normalbutyrylbenzamidine* by dissolving the butyrylbenzimidoethyl ester in dilute alcoholic ammonia in the same manner as benzoylbenzamidine was obtained. The product obtained, crystallized from water, melted at 126°–127°, and a nitrogen determination gave:

	Calculated for Butyrylbenzamidine.	Calculated for Benzamide.	Found. I.	Found. II.
N	14.7	11.57	11.71	11.74

The material thus obtained had all the properties of benzamide. It was found later that acetylbenzimido and propionylbenzimido esters by a similar treatment also give benzamide.

Normalbutyrylphenylbenzamidine. — Butyrylbenzimidoethyl ester reacts with aniline on warming, and the solid thus obtained on crystallizing from absolute alcohol separated in the form of colorless prisms and melted at 137°. A nitrogen determination gave:

	Calculated for $C_{17}H_{18}N_2O$.	Found.
N	10.52	10.53

An attempt to prepare *normalbutyrylmetanitrophenylbenzamidine*, by warming metanitraniline and butyrylbenzimidoethyl ester in molecular proportions, resulted in the formation

of a yellow varnish, which has stood for months without depositing crystals. Acetylbenzimidoethyl ester combines with isobutyl amine, and propionylbenzimidoethyl ester combines with allyl amine. Heat is evolved in both cases. The products formed are oils which have not been further investigated.

NEW HAVEN, May, 1898.

ON THE NON-EXISTENCE OF FOUR METHENYL-PHENYLPARATOLYL AMIDINES.*

[SECOND PAPER.]

BY H. L. WHEELER AND T. B. JOHNSON.

IT might be expected that amidines containing two different radicals attached to the different nitrogen groups would exist in more than one form. For example, theoretically, two structurally different benzenylphenylparatolyl amidines might exist:

$$C_6H_5C\begin{matrix}\diagup NHC_6H_5\\ \diagdown\!\!\diagdown NC_7H_7\end{matrix} \quad \text{and} \quad C_6H_5C\begin{matrix}\diagup\!\!\diagup NC_6H_5\\ \diagdown NHC_7H_7\end{matrix}$$

These, since they contain the grouping (R)R′C=N—R″, might be obtained in the form of geometrical isomerides.

In the case just cited Pechmann † believed that he obtained two isomeric amidines, when, by the action of aniline on benzparatolylimide chloride, he obtained an amidine melting at 133°, while from benzphenylimide chloride and paratoluidine an amide melting at 128° was formed. These two products were so much alike in properties and behavior that only the difference in the melting-points prevented the recognition of their identity. This doubt, however, disappeared when Marckwald ‡ showed that the melting-points are practically identical when the amidines are crystallized from absolute alcohol. Moreover, the chlorides and picrates agree in melting-points. Pechmann § then thoroughly examined a number of mixed amidines, prepared by methods which, if the reacting

* Amer. Chem. Jour., xx, No. 10.
† Ber. d. chem. Ges., xxvii, 1701.
‡ Ann. Chem. (Liebig), cclxxxvi, 348.
§ Ber. d. chem. Ges., xxviii, 869, 2363; Ibid, xxx, 1779 and 1783.

substances reacted by double decomposition, would have yielded isomers, but he found that the resulting amidines were invariably obtained in only one form. Then followed the surprising result of R. Walther. He described the preparation of methenylphenylparatolyl amidine,

$$C_6H_5N{=}CH{-}NHC_7H_7 \quad \text{or} \quad C_6H_5NH{-}CH{=}NC_7H_7,$$

by four methods. Each method that he tried gave a new amidine, according to him, and these amidines were supposed to be isomers.

One of us was induced to examine Walther's products solely because his speculations, involving direct double decomposition, seemed incredible. The results obtained by crystallizing Walther's products have already been published.*

It was found that products melting near the temperatures given by Walther could be prepared, but these did not behave like pure substances, since on crystallizing a sufficient number of times the melting-points rose in each case. In one case (I in table beyond) the melting-point finally coincided with that of methenyldiphenyl amidine; in another (II in table beyond) with methenyldiparatolyl amidine. In the other two cases (III, IV) the melting-points became almost identical.

Since these results appeared Zwingenberger and Walther † have again published the original paper with the addition of a more detailed account for the preparation of the different products, and have added along with other material the melting-points of the salts they examined.

In this last article they admit that one of their products (III) passes into the other (IV), "durch Erhitzen in Petroläther." In spite of this fact, previously shown by one of us (they ignore the results obtained by crystallization), Zwingenberger and Walther still maintain that these compounds are different amidines and that four methenylphenylparatolyl amidines exist. The method of preparation of these products,

* Amer. Chem. Jour., xix, 367.

† J. prakt. Chem., lvii, 209.

the salts and melting-points, as found by these authors, are given in the following table:

Results of Zwingenberger and Walther.

Preparation.	M. P. of Product.	M. P. of $PtCl_4$ Precipitate.	M. P. of Picrate.
I. By fusing together methenyldiphenyl amidine and *p*-toluidine	120°	213°	178°
II. By warming in alcohol methenyldi-*p*-tolylamidine and $C_6H_5NH_2.HCl$	132°	127° *	209°
III. From formtoluide, aniline, and PCl_3	98°	207°	196°
IV. From formanilide, *p*-toluidine, and PCl_3	102°	218°	193°

From the work done by one of us we knew that Walther's products I and II contained unaltered methenyldiphenyl and methenyldi-*p*-tolyl amidines respectively. It only remained to mix with these amidines what one might expect to get, *i. e.*, either one of the products obtained in III or IV, to solve the mystery of the four methenylphenylparatolyl amidines.

Product, M. P. 120°. — By mixing 8 parts methenyldiphenyl amidine (m. p. 135°) with 5.5 parts of methenylphenylparatolyl amidine (m. p. 98°–101°) and crystallizing this mixture once from petroleum ether, a product identical in every respect with the so-called methenylphenylparatolyl amidine of Zwingenberger and Walther can be prepared. The melting-point, behavior, appearance, all agree with the material prepared according to their directions, and the salts obtained from this mixture conform with surprising exactness with those prepared by the methods of Zwingenberger and Walther. (See I *a* in table beyond.)

Product, M. P. 132°. — By mixing 3 parts methenyldiparatolyl amidine (m. p. 140°) with one part of methenylphenyl-

* Probably misprint in Z. and W.'s article, and is intended for 217°.

paratolyl amidine (m. p. 98°–101°), and crystallizing the mixture once from petroleum ether, the so-called methenylphenylparatolyl amidine of Zwingenberger and Walther, melting at about 132°, can be obtained. The close agreement of these mixtures with the supposed amidines of Zwingenberger and Walther is shown by comparing the following table with I and II above:

*Mixtures Prepared by Us.**

		M. P.	$PtCl_4$ Precipitate.	Picrate.
I *a*.	8 parts methenyldiphenyl amidine and 5.5 parts methenylphenylparatolyl amidine	119°–124°	213°	177°–1789
II *a*.	3 parts methenyldi-*p*-tolyl amidine and 1 part methenylphenylparatolyl amidine	131°–133°	216°	209°

From this it is conclusively proved that Walther's amidines melting at* 120° *and* 132° *are mixtures, and are therefore to be

* It is unnecessary to describe here the various mixtures or proportions we experimented with. Within fairly wide limits the same results are obtained, so that the quantity of solvent is not given. A little more of the high-melting amidine raises the melting-point of the mixture, while more of the compound melting at 98°–101° lowers the same. It is interesting to note that the lower-melting constituent that we used melts lower than the mixture in both cases; no evidence of melting could be detected in the mixture below the figures given, and that, while the product melting at 98°–101° usually separates from ligroïn or petroleum ether in the form of needles, nevertheless, when mixed with methenyldi-*p*-tolyl amidine, which separates in prisms, only the prisms form, at least at first. A product prepared according to Walther's fourth method, which usually forms prisms, melted at 105°. When mixed with methenyldiphenyl amidine gave needles melting at 120°–125°. We now have the explanation of Walther's results, in regard to the different crystalline forms of the products melting at 98° and 102°. The material simply contains small quantities of other amidines which not only affect the melting-point, but determine what form shall result, either needles or prisms.

We will further examine these points later in other cases. What seems to be the best explanation of these curious facts is that the amidines form isomorphous mixtures, which, as experience teaches us, can only very slowly be separated by repeated crystallizations.

stricken from the literature. Since the same methenylphenylparatolyl amidine can be used in both of the above mixtures, it follows that ***only one mixed amidine results when Walther's first and second methods are followed.*** When, in the above mixtures, in place of the product melting from 98° to 101° the material prepared according to Walther's fourth method is used, almost the same melting-points are obtained both in the case of the duplicated "amidines" and their salts. It follows, therefore, that ***these products obtained by the third and fourth methods contain the same amidine; that there is therefore no proof of a direct double decomposition in these reactions; and that at the present time only one methenylphenylparatolyl amidine is known.***

Moreover, it may be stated that Walther determines structure by the method of preparation of amidines * in spite of the fact that Pechmann has shown, in numerous cases, that this is impossible. He states that from formanilide, paratoluidine, and phosphorus trichloride the following amidine must be formed, $C_6H_5NH-CH=NC_6H_4CH_3$. In other words, the action, according to him, must take place as follows:

$$HC\begin{cases}NHC_6H_5\\ \boxed{OH_2}NC_6H_4CH_3\end{cases} \rightarrow \quad HC\begin{cases}NHC_6H_5\\ NC_6H_4CH_3\end{cases}.$$

That the reaction does not proceed in this manner is shown by the fact that formanilide, methylaniline, and phosphorus trichloride give an excellent yield of methenylmethyldiphenyl amidine. Indeed, this appears to be a smoother reaction than when primary amines are used (see below):

$$HC\begin{cases}NHC_6H_5\\ O+\begin{matrix}CH_3\\ H\end{matrix}>NC_6H_5\end{cases} \rightarrow \quad HC\begin{cases}NC_6H_5\\ N<\begin{matrix}CH_3\\ C_6H_5\end{matrix}\end{cases}.$$

In this case it is impossible for the reaction to proceed as Walther states.

This reaction in the case of primary amines is altogether

* J. prakt. Chem., lv, 43; Ibid., lvii, 229.

too violent to be used to decide delicate cases of isomerism. Indeed it takes place with such energy that it has never happened in our work that the products obtained by one and the same method show even approximate agreement in their melting-points on crystallizing the same number of times. In one case in an attempt to prepare Walther's amidine melting at 98°, a product was obtained, which, after seven crystallizations from ligroïn, did not melt above 86°. In another attempt to prepare Walther's product melting at 102°, the only approximately pure product we could isolate was an amidine. This, however, did not melt at 102°, after five crystallizations, but from 134° to 135°. If the compound had separated in the form of needles, it would have been identified as methenyldiphenyl amidine; it was, however, probably methenyldiparatolyl amidine, but the quantity was too small to enable us to decide this point. Again, in one preparation of the compound melting at 102° a product was obtained that melted at 105°.

The conclusion from these results is that Walther's amidines said to melt at 98° and 102° (none of his amidines, as obtained by us, melted sharply), undoubtedly contain more or less of these impurities which caused the observed variations in melting-points.

Eight years ago it was found by Comstock and Wheeler, although the results were not published, that phenylformimidomethyl ester and metanitraniline gave the same methenylphenylmetanitrophenyl amidine as metanitrophenylformimidomethyl ester and aniline. Since these reactions take place at ordinary temperature, this method of studying possible isomers here is by far the best that has yet been employed. We propose to prepare methenylphenyl-*p*-tolyl amidine by similar methods, and determine how far the pure product differs from Walther's compounds.*

* Since the above was written, we have prepared this amidine by these methods, and find that it melts at 86°, and also that all the products described by Walther as methenylphenyl-*p*-tolyl amidines are, without exception, mixtures.

Methenylmethylphenylamide-phenylimidine, $C_6H_5(CH_3)N—CH=NC_6H_5$.—This amidine has been prepared now by three methods.

I. It was first obtained by Comstock and Wheeler * by mixing monomethylaniline with methylisoformanilide.

II. It has been obtained by us by adding a mixture of monomethylaniline and formanilide, in molecular proportions, to an excess of phosphorus trichloride. After the reaction the excess of phosphorus trichloride was poured off, and the residue treated with pounded ice. On standing the material dissolved, and to the cold solution cold sodium hydroxide was added. This precipitated an amber-yellow oil, which was extracted with ether and dried over calcium chloride. The ether was then evaporated, and the oil distilled at 25 mm. pressure. It began to boil at about 95°, then the temperature rapidly rose to 219°, when from 219° to 220° all but a few drops of material was collected. The first portion contained unaltered (?) material, while the portion boiling between 219° and 220° consisted of almost pure amidine. From 10 g. of formanilide, 4.5 g. of low-boiling, and 12.1 g. of material boiling within one degree were obtained. The material thus obtained had a slight odor of phenylisonitril. It was redistilled at 30 mm. and again at 26 mm. pressure. That it was not decomposed by this treatment is shown by the fact that it boiled constantly at this pressure from 218.5° to 219°. It still had an odor of isonitril, but this was present only in very small quantity.

III. In spite of the failures of Zwingenberger and Walther to prepare this amidine from methenyldiphenyl amidine by the action of methyl iodide, it can also be obtained in this way, but the preparation by this method is not to be recommended, as the yield, as determined by one experiment, is not good. We observed its formation when 10 g. of methenyldiphenylamidine were heated with an excess of methyl iodide to 135°–140° for seven hours. After evaporating off the excess of methyl iodide, a sticky, colorless residue was obtained.

* Amer. Chem. Jour., xiii, 518; Beilstein [3], ii. 346.

This was shaken thoroughly with ether and water. The ether took up the color and the aqueous solution was only pale yellow. A solid residue remained that did not dissolve. This proved to be the hydrogen iodide salt of unaltered amidine. The aqueous solution was treated with cold sodium hydrate, and the resulting oil separated, dried, and distilled at 30 mm. pressure; 2 g. of colorless oil came over below 226°, mostly dimethylaniline, then 3.5 g. of material, the greater portion distilled constantly at 226°, while above this 1.3 g. of thick oil remained. The portion boiling at 226° was not pure, however; it had the odor of isonitril, and deposited on standing, or when treated with ligroïn, crystals of unaltered methenyldiphenyl amidine. The ligroïn solution gave the salts described below.

Methenylmethylphenylamide-phenylimidine prepared by any of these three methods is a pale yellow, almost colorless, oil which in a freezing-mixture (−15°) gets thick and pasty, but could not be solidified. It is readily soluble in cold petroleum ether and the ordinary solvents. When concentrated hydrochloric acid is added to the oil, it gives the solid hydrochloride.

The Hydrochloride, $C_{14}H_{14}N_2HCl$. — This is best prepared by dissolving the amidine in petroleum ether and passing in dry hydrogen chloride. The precipitate crystallizes from absolute alcohol in large transparent colorless rhombohedrons or thick tables. It melts with decomposition at about 228°. A chlorine determination in the same prepared from the material obtained by the second method gave:

	Calculated for $C_{14}H_{14}N_2HCl$.	Found.
Cl	14.4	14.3

This salt is very soluble in water, and decomposes on standing in alcoholic solution.

The *Gold Chloride Double Salt*, $C_{14}H_{14}N_2HCl.AuCl_3$, has well-characterized properties, and easily serves to identify the amidine. It separates from alcohol by adding water in yellow,

six-sided plates with growth markings parallel to the edges. Prepared from material obtained by any of the above methods, it melted sharply at 145° (as previously described). A portion made from material obtained by the second method above gave the following result:

	Calculated for $C_{14}H_{14}N_2HCl.AuCl_3$.	Found.
Au (196.7) . .	35.7	35.3

NEW HAVEN, October 20, 1898.

ON THE REARRANGEMENT OF IMIDO-ESTERS.*

By H. L. WHEELER and T. B. JOHNSON.

The fact that the silver salts of the amides give imido-esters with alkyl halides was observed simultaneously, in the year 1890, by Tafel and Enoch † and by Comstock.‡ As we had occasion to prepare ethyl phenylimidoformate, $HC \begin{smallmatrix} \nearrow NC_6H_5 \\ \searrow OC_2H_5 \end{smallmatrix}$, by their method, and, wishing to avoid the slow process of warming silver formanilide suspended in ether with ethyl iodide for several days, we heated a portion of the silver salt to 100° in a closed tube with an excess of ethyl iodide. An oil was thus obtained which did not contain a trace of the expected imido-ester. The entire reaction-product was *N*-ethylformanilide,

$$H-C \begin{smallmatrix} \nearrow N < {C_6H_5 \atop C_2H_5}. \\ \searrow\!\!\!\searrow O \end{smallmatrix}$$

In order to assure ourselves that our material was not at fault, we boiled another portion of the same sample of silver salt, in an open vessel, with an ether solution of ethyl iodide, and got an excellent yield of the sought-for isomeric imido-ester.

This "tautomeric" reaction of the silver salt with ethyl iodide is remarkable, since the difference of conditions in the two cases cited is so small, — a difference of temperature less than 65° and only slight increase in pressure in the case of the reaction in the closed tube.§

* Amer. Chem. Jour., xxi, No. 3.

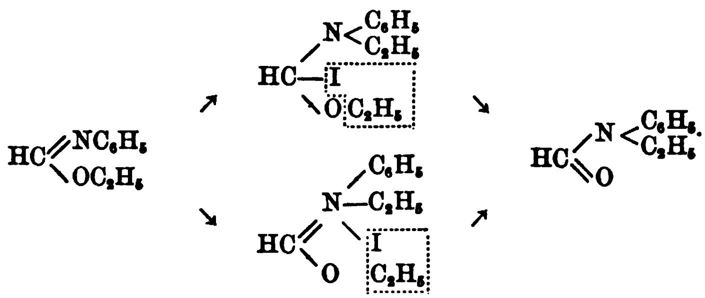
† Ber. d. chem. Ges., xxiii, 103 and 1550.

‡ Ibid., xxiii, 2274 and R. 659; also Amer. Chem. Jour., xiii, 514.

§ These striking results show that the method of preparation of a compound proves nothing in regard to its structure, and that arguments con-

Another portion of the same salt was heated again in a closed tube to 100°, as in the previous experiment, except that in this case a little less than the calculated amount of ethyl iodide was used, when little or no imido-ester was obtained.

These facts suggested that in the case of the reactions in the closed tube we have not a single reaction but a set of reactions. The first and intermediate product, the imido-ester, under the conditions of the experiment, reacts further with the ethyl iodide to give *N*-ethylformanilide. This must take place by addition in either of the following two ways:



That is, ethyl iodide is either added to the carbon and nitrogen that are doubly linked together, or entirely to the nitrogen, and then separates again in another manner, as indicated by the dotted lines.

That this is the course of the reaction is shown by the fact that benzimidoethylester, prepared by Pinner's method from benzonitril, when heated with ethyl iodide at 100°, gives practically nothing but ethylbenzamide:

cerning structure, based solely on the compounds formed in a reaction, have no weight. In the sodium salts of the amides the metal is universally represented as attached to nitrogen simply because these salts give nitrogen alkyl compounds with alkyl halides. That the metal is attached to nitrogen in these compounds is improbable. The above reactions show that slight changes in conditions may produce opposite results, and the difference in conditions when alkyl halides act on sodium salts on the one hand and on silver salts on the other, is certainly great — greater, at least, than is necessary to produce the opposite results in the case of the same material, *i. e.*, the silver salts.

$$C_6H_5\begin{array}{l}\nearrow\!\!\!\!\nearrow NH\\ \searrow OC_2H_5\end{array} \rightarrow C_6H_5C\begin{array}{l}\nearrow NHC_2H_5.\\ \searrow\!\!\!\!\searrow O\end{array}$$

The reaction taking place as shown above has the effect of simply transferring the ethyl from its union with oxygen to the nitrogen.

The tautomeric reaction in these cases, as in others, is undoubtedly nothing but a reaction by addition.

The above cases are the first that have been observed where a silver salt of an acyclic amide, anilide, or imido-ester gives nitrogen derivatives with alkyl iodides.* The behavior of the silver salts and imido-esters with alkyl halides under pressure and at a somewhat elevated temperature is analogous to their behavior with acyl chlorides in the cold. It was shown in previous papers † on the compounds in question, that the silver and mercury salts of the anilides, and the corresponding imido-esters give the same diacylanilides, and that nitrogen-substituted derivatives resulted in each case.

The above action of ethyl iodide on silver formanilide explains the behavior of acyl chlorides with the silver salts — a "tautomeric" reaction when compared with our previous knowledge of the action of alkyl halides. It would seem that silver formanilide, for example, reacts, giving an acyl derivative, as follows:

$$HC\begin{array}{l}\nearrow\!\!\!\!\nearrow NC_6H_5\\ \searrow OAg\end{array} \rightarrow \overset{\textbf{A.}}{HC\begin{array}{l}\nearrow\!\!\!\!\nearrow NC_6H_5\\ \searrow O.COCH_3\end{array}} \rightarrow \overset{\textbf{B.}}{HC\begin{array}{l}\nearrow N\begin{array}{l}\nearrow C_6H_5\\ -COCH_3\\ \searrow \boxed{\begin{array}{l}Cl\\ COCH_3\end{array}}\end{array}\\ \searrow O\end{array}}$$

* Pinner, in his work "Die Imidoäther," states that an attempt to replace the imide hydrogen in benzimidoisobutylester by heating the ester to 100° with ethyl iodide led to no result. He obtained an abundant separation of cyaphenin with a small amount of resin. This result was probably due to the fact that Pinner's ester was not purified by distillation under diminished pressure. When these esters are thus purified some of them do not decompose, but can be distilled at ordinary pressure, as shown by Bushong, Amer. Chem. Jour., xviii, 490, and in previous papers from this laboratory.

† Wheeler and Boltwood, Amer. Chem. Jour., xviii, 381; Wheeler and McFarland, Ibid., xviii, 540; Wheeler, Ibid., xviii, 695; Wheeler and Walden, Ibid., xix, 129; Wheeler and Metcalf, Ibid., xix, 217; Wheeler, Walden, and Metcalf, Ibid., xx, 64.

The first acyl derivative (A), being unstable, reacts further by addition as above (B), then acetyl chloride separates, the stable form, $O{=}\overset{H}{\overset{|}{C}}{-}\overset{COCH_3}{\overset{|}{N}}{-}C_6H_5$, results. The curious fact that silver benzamide gives with benzoyl chloride benzonitril and benzoic acid, and not dibenzamide, confirms this supposition. The first reaction of the silver salt is a direct replacement of silver by the acyl group. This arrangement being unstable the compound formed decomposes as follows:

$$C_6H_5C\left\langle\begin{matrix}N\ H\\ OCOC_6H_5\end{matrix}\right. .$$

It may, however, be stated in general that compounds of the formula $RO\overset{R'}{\overset{|}{C}}{=}\overset{R''}{\overset{|}{N}}$ are more or less unstable, and readily pass into the isomeric form $O{=}\overset{R'}{\overset{|}{C}}{-}\overset{R''}{\overset{|}{N}}{-}R$. The ease with which this takes place depends on the character of the groups R, R′, and R″. It is therefore not improbable that with suitable groups and the proper regulations of conditions pseudoamides, $R'C\left\langle\begin{matrix}NR\\ OH\end{matrix}\right.$, and imidoacylanhydrides, $R'C\left\langle\begin{matrix}NR''\\ OCOR'\end{matrix}\right.$, which at present are unknown among acyclic compounds, may be prepared.

Experimental Part.

N-Ethylformanilide from Silver Formanilide.—25 g. silver formanilide dried over sulphuric acid and which on analysis gave 47.86 per cent of silver (calculated 47.41 per cent), were heated with 22 g. of ethyl iodide* to 95°–100° for six

* In the experiments in closed tubes we invariably weighed our ethyl iodide in a thin glass tube, which was sealed up as soon as weighed. This, with the imido-ester, was introduced into the larger tube used in heating, and after this tube had been sealed and cooled, the smaller tube was broken by shaking. In this way we avoided loss by evaporation, and the otherwise unavoidable separation of iodine that always accompanies the sealing of tubes containing ethyl iodide.

hours. An oil resulted which was extracted from the silver iodide by means of dry ether. This gave, on distilling, a product boiling from 257° to 267°. (Ethyl phenylimidoformate boils from 213° to 215° at ordinary pressure.) This oil was twice distilled. It evidently decomposes to some extent. Two fractions were finally obtained. The first, which was clear and colorless, boiled from 259° to 263°; the second from 263° to 266° (barometer 772 mm.), the whole material boiling within 7°, except a small residue left in the distilling-bulb. The absence of ethyl phenylimidoformate was shown, not only by the boiling-point of the material, but also by mixing with ortho- and paratoluidine, when no amidides were found. A nitrogen determination in the clear, colorless, inodorous oil (no isonitril odor, hence entire absence of formanilide) gave:

	Calculated for $HCONC_2H_5.C_6H_5$.	Found.
N	9.40	9.70

The material is therefore isomeric with the expected ethyl phenylimidoformate. Pictet and Crépieux* give the boiling-point of ethylformanilide as 258° at 728 mm. The fact that our material boiled, for the most part, higher than this is due to the difference in barometic pressure.

That our material was ethylformanilide is shown by the fact that on warming with hydrochloric acid and a little alcohol the formyl group separated as ethyl formate, and the resulting solution, on evaporation to dryness, gave a crystalline residue which, when pressed on paper and dried in the air, melted (not sharply) at 173°. Reynolds† states that the melting-point of ethylaniline hydrochloride is from 172° to 175°. This, on dissolving in ice-water, gave, with potassium nitrite, the characteristic nitroso-compound of ethylaniline. There is, therefore, no doubt, that the entire reaction-product was ethylformanilide.

In order to determine whether the silver salt of formanilide reacts more readily with ethyl iodide than the imido-ester under the conditions of the reaction in the closed tube, we

* Ber. d. chem. Ges., xxi, 1108.

† Jour. Chem. Soc., lxi, 455.

heated 15.45 g. of silver formanilide with 9.6 g. of ethyl iodide (about 1 g. less than molecular proportions) to the same temperature and for the same length of time as in the previous experiment. This gave an oil, but not a trace came over at the boiling-point of the imido-ester. It began to boil at about the same temperature as the product of the previous experiment, but the quantity was too small to give a constant boiling-point. The first few drops that came over were mixed with aniline, and then sufficient diphenylformamidine for a melting-point determination was obtained. This shows that ethyl phenylimidoformate is more readily acted on in closed tubes than the silver salt.

In another experiment 25 g. of silver formanilide, the same preparation as that used above, and considerable excess of ethyl iodide, were warmed in ether for three days on the water-bath; not all the salt was acted on at this time, but, nevertheless, we obtained about 8 g. of ethylphenylimidoformate, boiling from 213° to 217°. The higher boiling material was by far the smallest part. This, decomposed with hydrochloric acid and evaporated to dryness, gave a solid mass which was taken up in water, filtered from resin, and then nitrous acid precipitated the nitroso-compound of ethylaniline. It seems, therefore, that ethyl phenylimidoformate suffers rearrangement, to some extent, at ordinary pressure and at the temperature of boiling ether.

N-Ethylbenzamide from Ethyl Imidobenzoate.—10 g. of ethyl imidobenzoate and 16 g. of ethyl iodide were sealed up and heated to 100° for eight hours, then two or three hours at 130°–160°. The contents of the tube, after evaporation of the ethyl iodide, distilled almost entirely from 176° to 184° at 20–21 mm. pressure. A few drops distilled below 176°. This proved to be benzonitril. The chief product, weighing about 7 g., was redistilled at ordinary pressure, when it practically all boiled from 295° to 296°. This perfectly colorless oil deposited some crystals. The whole was then taken up in benzene and filtered from a small amount of material crystallizing in plates and melting from 123° to 126°

(benzamide (?)). The benzene solution was evaporated and the oil redistilled. It boiled from 295° to 298° and, on standing over night, deposited a mass of thick, colorless prisms. These, pressed on paper and freed from a little inodorous oil, melted from 69° to 70°. (The oil is perhaps

$$C_6H_5C\begin{cases}\!\!{=}NC_2H_5\\ \!\!-OC_2H_5\end{cases} \quad \text{or} \quad C_6H_5C\begin{cases}\!\!-N{<}\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\\ \!\!{=}O\end{cases}.$$

It will be investigated later.) The material was crystallized from dilute alcohol, when beautiful, long, flattened, colorless prisms developed from the oil which first separated. These melted at about 69°. The melting-point of ethylbenzamide is usually given as 68°–69°. A nitrogen determination gave the result I, below.

In another experiment, when an excess of imido-ester was used, the quantity of ethyl iodide being in the proportion of 2 molecules of the ester to 1 molecule of the iodide, the chief product boiled from 298° to 299°. This was analyzed without being allowed to stand. It was free from crystals at first, but on standing solidified. The result on analysis (II, below) shows that it is practically identical with the solid I.

	Calculated for $C_6H_5CONHC_2H_5$.	Found. I.	Found. II.
N	9.40	9.11	9.47

The melting-point, appearance, behavior, and analysis therefore agree with those of ethylbenzamide, but Gattermann and Schmidt * give the boiling-point of this compound as 256°–260°. To settle this point we prepared ethylbenzamide by the Schotten-Baumann reaction, and found that with 14 g. of material the entire product boiled at 762 mm. pressure from 298° to 300°. This material is identical with the product from ethyl imidobenzoate in all its properties, and the boiling-point given by the above authors is far from correct.

A quantitative determination of the products formed in the latter of the above experiments was made as follows: When

* Ann. Chem. (Liebig), ccxliv, 50.

15 g. of ethyl imidobenzoate (2 molecules) were heated in a closed tube with 7.85 g. of ethyl iodide (1 molecule) for eight hours, a somewhat thick oil or solution resulted which contained minute crystals in suspension. The contents of the tube were diluted with dry ether, and the turbid solution filtered. The melting-point of the needles, after they were washed with ether, showed that the material was a mixture or impure. It showed signs of melting at 120° and was completely melted at 203°. It had the appearance of cyaphenin. The quantity of this material was insignificant, less than 0.2 g. On evaporating the ether solution an oil was obtained which was distilled at 18–19 mm. pressure. Three portions were then obtained: (1) below 170°, 1 g.; (2) 170°–178°, 9.1 g.; and a residue in smaller quantity above 178°, which soon solidified on cooling.

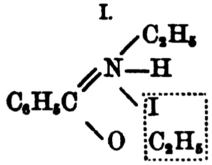
The first fraction proved to be mostly benzonitril; the second or greater portion was redistilled at 762 mm. pressure, when it practically all boiled from 298° to 299°. It was obtained as a strongly refracting colorless oil which, on standing, soon solidified, but not completely, giving beautiful large crystals of ethylbenzamide. The residues from this distillation and that from the distillation under diminished pressure were dissolved in ether and the ether then evaporated. This residue weighed 4.5 g. It appeared to consist of a mixture of benzamide and ethylbenzamide. It melted at about 60°. The material, crystallized from benzene, melted from 120° to 126°. On crystallizing from water it separated in the form of plates and melted at 128°. The quantities of the different products, formed in the above experiment, is therefore about as follows:

	G.
Benzamide and ethylbenzamide	4.5
Ethylbenzamide (and diethylbenzamide (?)) .	9.1
Benzonitril	1.0
Cyaphenin	0.2

From this it is apparent that the chief reaction is a rearrangement of the ethyl group from oxygen in the imido-ester to the nitrogen.

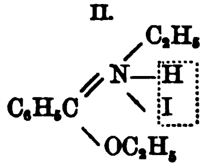
The formation of benzamide is to be explained by the decomposition of ethyl imidobenzoate hydriodide, which is known to decompose into ethyl iodide and benzamide when heated. The formation of this ethyl imidobenzoate hydriodide is due to the separation of hydriodic acid from the addition-product which, as above stated, must be formed as an intermediate product. The reaction of ethyl iodide on ethyl imidobenzoate, therefore, proceeds in two ways, or, in other words, the primary addition-product separates chiefly ethyl iodide (I, below), and to a lesser extent a portion decomposes separating hydrogen iodide (II), which then unites with the unaltered imido-ester:

I.



and

II.



The ethyl ethylimidobenzoate resulting from the decomposition II is then rearranged with ethyl iodide yielding diethylbenzamide, or remains unaltered, so that one or both of these compounds constitute the oil which accompanies, in small amount, the crystals of ethylbenzamide.

Diethylbenzamide is known to be an oil. The other compound, ethyl ethylimidobenzoate, has not yet been prepared.

We are now engaged in preparing this and similar compounds, in order to determine more positively what the by-products in these reactions are, and we intend to examine the rearrangement of other imido-esters, in general, more thoroughly. We wish to reserve this field for ourselves.

NEW HAVEN, November 1, 1898.

ON THE REARRANGEMENT OF THE THIONCARBAMIC ESTERS.*

BY H. L. WHEELER AND BAYARD BARNES.

IN the year 1849 Debus † found that when xanthogenamide, sulphourethane, sulphocarbamic ethyl ester or ethyl thioncarbamate ‡ is heated, it is decomposed into ethyl mercaptan and cyanuric acid. This is, perhaps, not what would be expected of a compound having the structure $H_2NCS.OC_2H_5$. Its structure is shown, however, by its method of preparation from the xanthogenic esters and ammonia:

$$C_2H_5OCS.\boxed{SC_2H_5 \quad H}NH_2 = C_2H_5OCS.NH_2 + HSC_2H_5.$$

With alkali it is decomposed normally, according to Debus,§ into alcohol and sulphocyanate. C. Liebermann,‖ commenting on this behavior in 1881, states: "Es ist nicht unmöglich, dass man diese Reaction durch eine Umlagerung vielleicht in das von Salomon ¶ entdeckte carbonylsulfäthylamin [ethyl thiolcarbamate $H_2NCO.SC_2H_5$] erklären muss, wofür auch der Umstand spricht, das die einmal begonnene Reaction von selbst fortschreitet."

Liebermann, however, did not test this explanation or assumption.

It seemed to the writer that if the thioncarbamic esters are capable of rearrangement into the isomeric thiol derivatives this reaction would be aided by alkyl iodides. The iodides

* Amer. Chem. Jour., xxii, No. 2.

† Ann. Chem. (Liebig), lxxii, 18.

‡ In naming these substances the writer has employed the Geneva nomenclature *thion* and *thiol*. By this means the position of the sulphur can best be indicated, *thion* being used for compounds containing the group —CS.OR, and *thiol* for those containing the group —CO.SR.

§ Ann. Chem. (Liebig), lxxv, 149.

‖ Ibid., ccvii, 165.

¶ J. prakt. Chem. [2], vii, 256.

would unite with the esters forming, at least, an intermediate addition-product — somewhat analogous to the sulphonium compounds — which would then give up alkyl iodide in another manner.

This seemed probable, as Jeanjean* found that dithiocarbamic ethyl ester gives a crystalline compound with ethyl iodide, $H_2NCS.SC_2H_5 + C_2H_5I$, while the work of Claus,† Bernthsen,‡ Wallach,§ and others has shown that the thioamides in general form similar addition-products with alkyl halides.

We therefore heated 10 g. of ethyl thioncarbamate with 5 g. of ethyl iodide for a number of hours in a sealed tube, at 92°–96°. On cooling and opening the tube ethyl mercaptan and a compound having the properties of cyanuric acid were obtained. Under these conditions the reaction had proceeded as Debus found when the amide was submitted to distillation. Evidently this treatment was too energetic.

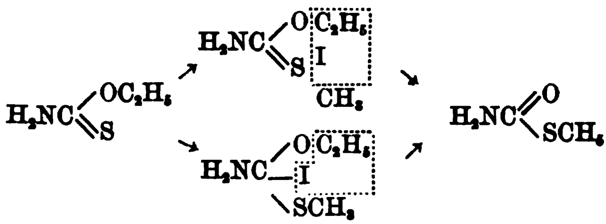
We then tried the action of ethyl iodide at ordinary temperature, when it was found that the rearrangement took place readily.

With methyl iodide the rearrangement is most striking. When methyl thioncarbamate (methyl xanthogenamide), melting at 43°, is mixed with a molecular proportion of methyl iodide, it dissolves, the temperature of the solution sinks, and then in a few minutes becomes warm enough to boil off the methyl iodide, and the whole solidifies to a shining mass of flattened prisms or plates. The material, after this treatment, melts at 105°–107°, and is, in fact, methyl thiolcarbamate, the carbonylsulfmethylamine of Blankenhorn.‖ The methyl group has been transferred from the oxygen to the sulphur, and the thion compound has been transformed into a thiol:

$$H_2NC\begin{matrix}{/\!\!/}S\\ \diagdown OCH_3\end{matrix} \quad \longrightarrow \quad H_2NC\begin{matrix}\diagup SCH_3\\ {\diagdown\!\!\diagdown}O\end{matrix}.$$

* Jahresb. (1866), 501.
† Ber. d. chem. Ges., viii, 41.
‡ Ann. Chem. (Liebig), cxcii, 56.
§ Ber. d. chem. Ges., xi, 1594.
‖ J. prakt. Chem., xvi, 379.

This interesting rearrangement is undoubtedly the result of a series of reactions, the alkyl iodide separating into its constituents, alkyl and iodine, the constituents being added to the sulphur, and then separating alkyl from the oxygen along with iodine from the sulphur. This, perhaps, is best shown by the behavior of ethyl thioncarbamate (ethyl xanthogen amide) with methyl iodide, the action taking place with the same ease as with the methyl compound. This may be represented in either of the following two ways:



That is, either the alkyl iodide forms a tetravalent sulphur addition-product or it is added to the double union between sulphur and carbon. At any rate, from ethyl thioncarbamate and methyl iodide, methyl thiolcarbamate and ethyl iodide are obtained.

We have prepared a series of thioncarbamic esters and find that they all undergo this change easily with alkyl iodides. This rearrangement, moreover, is not confined to the action of iodides. Ethyl bromide, and even ethyl chloride, converts ethyl thioncarbamate into ethyl thiolcarbamate.

It might be expected now that ethyl thioncarbamate with ethylene bromide would give the compound

$$H_2NCO.SCH_2.CH_2.Br.$$

This, however, is not the case. As commonly observed with ethylene bromide, both halogens react at once, and the ethylene ester of thiolcarbamic acid results,

$$H_2NCOSCH_2CH_2SCONH_2,$$

along with ethyl thiolcarbamate, the latter resulting from the action of ethyl bromide which is evolved in the reaction.

George Pinkus,* in his work on the action of trimethylene chlorobromide on thioamides, obtained, in the case of xanthogenamide, a product to which he assigns the empirical formula

$$C_4H_8NOS\frac{Br + Cl}{2}.$$

He states that in the reaction ethyl bromide was evolved and the product melting from 102° to 103° gave with potassium hydrate an offensive odor. It is now evident that in this experiment Pinkus had effected a rearrangement of the xanthogenamide without recognizing it, and that his product corresponds to a mixture of equal parts ω-chlor- and ω-brompropyl thiolcarbamates.

We have found that ethyl thioncarbamate reacts readily with chloracetic acid and other halogen compounds. These reactions will be described in a later paper. At present we have not examined the substituted thioncarbamic esters RNHCSOR′ and RNR″CSOR′, but we intend to do this later.

The above rearrangements, taking place as they do at ordinary temperatures, alter our views in regard to the structure of certain salts of thio- or sulphocarbamic acids. Neither thioncarbamic acid, $H_2NCS.OH$, or thiolcarbamic acid, H_2NCOSH, is known, and according to Beilstein † only salts of thiolcarbamic acid have been obtained.

The formation of the ammonium salt, when carbon oxysulphide and ammonia combine, ‡ is represented as follows:

$$COS + 2NH_3 = H_2NCO.SNH_4.$$

This thiol structure was established by the work of Fleischer,§ who found that the salt gives with ethyl bromide at 100°, ethyl thiolcarbamate. Fleischer, therefore, concluded that this result settled his controversy with Claus,‖ who considered the compound a thion derivative. Previously, Kretzschmar¶ assigned the thiol structure to this salt, chiefly because it

* Ber. d. chem. Ges., xxvi, 1077.

† Handbuch d. org. Chem. [3], i, 1258.

‡ Berthelot, Jahresb. (1868), 160.

§ Ber. d. chem. Ges., ix, 991.

‖ Ibid., ix, 723.

¶ J. prakt. Chem., vii, 475.

gives urea and hydrogen sulphide when heated. Schmidt* came to the same conclusion.

Since now the action of ethyl bromide cannot be used to distinguish between a thiol or thion structure in this class of substances, it seems to the writer that the view of Claus is the best; *i. e.*, the ease with which this salt is desulphurized points to the formula $H_2NCSONH_4$. This view is confirmed by the fact that $H_2NCS.OC_2H_5$ is readily desulphurized by silver nitrate, while $H_2NCOSC_7H_7$ gives a stable silver salt.

The action of ethyl bromide on this salt is therefore to be represented in precisely the same manner as shown above in the case of the thioncarbamic esters:

$$H_2NC\left\langle{}^{S}_{O.NH_4}\right. \rightarrow H_2NC\left\langle{}^{S.C_2H_5\boxed{Br}}_{O\boxed{NH_4}}\right. \rightarrow H_2NC\left\langle{}^{SC_2H_5}_{O}\right. .$$

The questions now arise: Is this reaction a general one for thion compounds? Will compounds of the structure ROCS.OR give ROCO.SR, and ROCS.SR be transformed into RSCO.SR? Do the salts of the thioncarbonic acids react tautomerically with alkyl halides?

With the exception of the above series and the alkyl sulphur derivatives of carbonic acid, little is known of the thion compounds containing the grouping — $CS.OC_2H_5$. One salt of thionethylcarbonic acid has been described. Klason† states that carbon sulphochloride, $CSCl_2$, and sodium ethylate give $C_2H_5OCSONa$. With this exception it is noteworthy that all the salts of thio- and dithiocarbonic acids hitherto described have the thiol structure assigned to them.

This work also suggests that under suitable conditions a rearrangement may perhaps be expected in the case of tetravalent sulphur compounds; for example, a shifting of alkyl from oxygen to sulphur may be expected in the case of the esters of the sulphinic acids thus giving sulphones:

$$R\text{—}S\left\langle{}^{O}_{OR}\right. \rightarrow R_2S\left\langle{}^{O}_{O}\right. .$$

* Ber. d. chem. Ges., x, 191.

† Ibid., xx, 2384.

The alkyl sulphites may be transformed into alkyl sulphonic esters, etc.

$$C_2H_5O—SO—OC_2H_5 \rightarrow C_2H_5SO_2OC_2H_5.$$

Preliminary experiments by Mr. T. B. Johnson with benzenesulphinic ethyl ester and by Mr. R. J. Donnelly with ethyl dithiocarbonate, $C_2H_5OCSSC_2H_5$, show that these compounds are not transformed under the same conditions as the thioncarbamic esters, there being little, if any, tendency of the former, less positive, molecules to undergo change with ethyl iodide.*

In the case of the alkali and ammonia salts of thioncarbonic acid the molecule is even more positive than in the case of the thioncarbonic esters; therefore it appears that these compounds should react tautomerically.

We wish to reserve for this laboratory the examination of these questions and the study of the rearrangement of thion derivatives with organic halogen compounds in general, and work along these lines is now in progress here.

Experimental Part.

The thioncarbamic esters were prepared in the usual manner by the action of ammonia on the dithiocarbonic esters, and the latter were prepared by means of ethyl bromide from the potassium xanthogenates.

* It seems that basicity plays an important part in these addition reactions. It is probably due to the basicity of the molecules that the salts of the sulphinic acids give sulphones, and that the salts of sulphurous acid give the unsymmetrical derivatives with alkyl halides. Owing to the acid character of the molecules, it appears improbable that the nitrites will be changed to the nitroparaffins by alkyl iodides. In the case of the more positive salts of nitrous acid, which act tautomerically, the behavior is precisely what would be expected of an addition-reaction. The higher alkyl iodides, which in general have less tendency to take part in addition-reactions, owing perhaps to stereochemical interference, give chiefly nitrites with these salts, while in the case of the lower halides the nitroparaffins result. In this connection the inertness of β-ethoxycrotonic ethyl ester may be mentioned. This compound can be heated with ethyl iodide for hours at 170°–180° without being converted into ethyl acetoacetic ester, and it can be boiled with benzoyl chloride and recovered unaltered.

Methyl Thiolcarbamate from Methyl Thioncarbamate. — 1 g. of the latter was mixed with 1.5 g. of methyl iodide. On dissolving the solution became cool, then warm, and the product separated in a solid mass of crystals melting at 105°–107°. On crystallizing from water it melted at 107°–108°.

Blankenhorn * obtained this compound from potassium sulphocyanide, methyl alcohol, and hydrochloric acid, but probably not in a pure condition, since he states that the melting-point lies betweeen 95° and 98°. In all other respects our compound agrees with Blankenhorn's description. In 20 per cent alcoholic solution it gave a yellowish-white, curdy precipitate with silver nitrate. Platinum chloride gave an orange-yellow, mercuric chloride a white, and cupric sulphate a dirty white precipitate. These precipitates did not alter on standing.

Methyl thiolcarbamate is easily soluble in ether and in alcohol, but less readily in water, from which it separates in large, shining, colorless plates that have a talc-like consistency. It is somewhat volatile with steam. Warmed with aniline, it evolves methyl mercaptan and ammonia and diphenylurea remains. This carbamate is identical in every respect with the following:

Methyl Thiolcarbamate from Ethyl Thioncarbamate. — The ethyl thioncarbamate used in this and other experiments melted at from 40° to 41° and not at 38°, as stated by Salomon.† It was purified by dissolving it in ether and precipitating with petroleum ether, when it was obtained in beautiful, square, thick tables.

When 5.5 g. of this material were dissolved in 10 g. of methyl iodide, the solution became cold, but on standing a few minutes heat was evolved, and a mass of plates separated. On crystallizing these from water they melted at 107°–108°. A nitrogen determination gave the following result:

	Calculated for $H_2NCO.SCH_3$.	Calculated for $H_2NCOSC_2H_5$.	Found.
N	15.38	13.33	15.84

* J. prakt. Chem. [2], xvi, 375.

† Ibid. [2], viii, 115.

It was found that the melting-points of methyl and ethyl thiolcarbamates are identical; they melted side by side at the same temperature in the same apparatus. In order, therefore, to confirm our analytical result and prove that methyl and not ethyl thiolcarbamate results in this reaction, Mr. W. M. Saunders performed the following experiment to determine whether our product with aniline gives methyl mercaptan (a gas) or ethyl mercaptan (a liquid boiling at 36°), and also to identify the products of the reaction. 2 g. of the product obtained by acting on ethyl thioncarbamate with methyl iodide were heated with about 2 molecules of aniline to 160° in an oil-bath, when over 350 c. c. of gas was obtained which was collected over water. Ammonia and the odor of mercaptan were noticed. The gas passed into a solution of mercuric cyanide gave a finely divided white precipitate, which, purified by means of alcohol, in which it is very difficultly soluble, melted with decomposition at 170°–175°. The residue left on heating was crystallized from alcohol, when diphenylurea was obtained melting at 234°–236°. There is, therefore, no doubt that methyl thiol carbamate is formed in the above reaction, and the action with aniline proceeds as follows:

$$CO\begin{array}{l}\diagup NH_2 \quad H\,HNC_6H_5\\ \diagdown SCH_3 \quad H\,HNC_6H_5\end{array} = CO\begin{array}{l}\diagup NHC_6H_5\\ \diagdown NHC_6H_5\end{array} + CH_3SH + NH_3.$$

Ethyl Thiolcarbamate from Ethyl Thioncarbamate. — When a portion of ethyl thioncarbamate (xanthogenamide) was dissolved in ethyl iodide, and the solution allowed to stand, a mass of silver-white plates remained after spontaneous evaporation of the iodide. These melted at 107°–108°. Another portion was allowed to stand only an hour, when the material melted below 60°; the rearrangement then not being complete, the solution was warmed on the water-bath, when it soon solidified. This rearrangement, therefore, takes place with greater difficulty than in the case of the methyl carbamate. The material in this instance, melting at 107°–108° and needing no purification, was simply pressed on paper and dried in the air. A nitrogen determination gave the following:

	Calculated for $H_2NCO.SC_2H_5$.	Found.
N	13.33	13.02

This product gave the reactions for "carboxylsulfäthylamin" as described by Konrad and Salomon.* Although, as stated, the melting-point of this compound is identical with that of the methyl derivative, a mixture of the two was found to melt below 89°.

In another experiment ethyl thioncarbamate (5 g.) and ethyl bromide (6 g.) were heated for an hour on the water-bath, when it was found that a rearrangement had taken place, the product being identical with the above.

Isopropyl Thiolcarbamate from Isoamyl Thioncarbamate.—10 g. of the latter were heated with 12 g. of isopropyl iodide on the steam-bath for two days. On cooling, a mass of crystals was obtained. These were washed with warm petroleum ether and crystallized twice from water, when the material was obtained in colorless rectangular plates melting at about 125°. A nitrogen determination gave:

	Calculated for $H_2NCOSC_3H_7$.	Found.
N	11.76	11.84

The behavior of this material with silver nitrate, mercuric chloride, copper sulphate, and platinum chloride is identical with that of isobutyl thiolcarbamate and the other members of this series.

Isobutyl Thioncarbamate was obtained by Mylius † from "isobutyldioxysulfocarbonat" and alcoholic ammonia. He states that it forms yellowish-white tables (from alcohol) melting at 36°. Blankenhorn ‡ obtained this mixed with the thiol compound by treating potassium sulphocyanide in isobutyl alcohol with hydrochloric acid. He describes his product as a yellow oil crystallizing at 6° and melting at 10°. Our compound prepared from $C_5H_{11}O.CS.SC_2H_5$ and alcoholic ammonia readily solidified, and on crystallizing once from ether and then from water, melted at 51°–53°. It forms a

* J. prakt. Chem., x, 35.

† Ber. d. chem. Ges., v, 976.

‡ J. prakt. Chem. [2], xvi, 380.

snow-white mass of plates, and a nitrogen determination gave the following:

	Calculated for $H_2NCS.OC_4H_9$.	Found.
N	10.52	10.40

Isobutyl thioncarbamate in dilute alcoholic solution gives with silver nitrate a white precipitate which soon turns black (difference from thiolisobutylcarbamate). Mercuric chloride gives a white precipitate which can be boiled with water without change of color. Copper sulphate gives a white precipitate which, when warmed, changes to black. Platinum chloride gives a yellow precipitate which, when warmed, decomposes.

Isobutyl Thiolcarbamate from Isobutyl Thioncarbamate. — 5 g. of the above material, melting at 51°–53°, were heated with 1 g. of isobutyl iodide, on the water-bath, for two hours, and on taking out a portion it was found to melt unaltered at 51°–53°. It was then heated in an oil-bath to 120° for several hours. On cooling, and crystallizing the material from water, it was then found to melt at 102°–103°. It thus separates in magnificent snow-white plates of extreme thinness. A nitrogen determination gave:

	Calculated for $H_2NCOSC_4H_9$.	Found.
N	10.52	10.45

Isobutyl thiolcarbamate closely resembles the other members of the thiol series. It is readily soluble in the ordinary solvents, except cold water, and it is volatilized with steam. Silver nitrate added to its dilute alcoholic solution produces a white precipitate which does not alter on standing. With mercuric chloride it behaves like the thion compound. With copper sulphate no precipitate is obtained in the cold, but on warming a white precipitate separates. Platinum chloride gives no precipitate in dilute solution.

Isoamyl Thiolcarbamate from Isoamyl Thioncarbamate. — Isoamyl thioncarbamate, as prepared in 1853 by M. W. Johnson * from "binoxysulphocarbonate of amyl" and ammonia was

* Quart. J. Chem. Soc., v, 142.

an oil. Our material also was obtained as an oil which refused to solidify on cooling. When heated (10 g.) with isoamyl iodide (5 g.) at 120°–130° for several hours, it was transformed slowly and less completely than the lower members of this series. The product, crystallized from hot water, formed extremely large, silver-white plates resembling thin slices of mica. It melted at 112°–113°, while Schöne * says that isoamyl thiolcarbamate forms plates melting at 107°, when prepared from the chloride $C_5H_{11}SCOCl$ and ammonia. A nitrogen determination gave:

	Calculated for $H_2NCO.SC_5H_{11}$.	Found.
N	9.52	9.16

Isoamyl thiolcarbamate does not differ in properties from the other members of the series. With silver nitrate, mercuric chloride, copper sulphate, etc., it behaves precisely like isobutyl thiolcarbamate.

Ethyl Thioncarbamate and Ethylene Bromide. — When 10 g. of the former and 37 g. of the latter were mixed, and heated on the steam-bath for three hours, ethyl bromide was evolved and, on cooling, a crystalline mass was deposited. It was purified by boiling with alcohol and water, which extracts ethyl carbamate, and was thus obtained as a crystalline powder which was quite difficultly soluble in the ordinary solvents. It was free from bromine, and a nitrogen determination gave the following:

	Calculated for $C_4H_8S_2N_2O_2$.	Found.
N	15.55	14.99

Ethyl Benzenesulphinate, $C_6H_5SO.OC_2H_5$, with Methyl and Ethyl Iodides. — The following negative experiments were performed by Mr. T. B. Johnson, to whom we wish to express our thanks. 4 g. of the ethyl ester were heated with 3.6 g. of ethyl iodide at 100°–110° for one hour, when no apparent reaction took place. On further heating, the material darkened, but it deposited no crystals when placed in a freez-

* J. prakt. Chem. [2], xxxii, 247.

ing mixture. Heated further for four hours at 130°–140°, considerable decomposition took place. The material, extracted with ether, washed with sodium hydroxide, dried, and evaporated, gave no solid material.

Ten g. of the ester were heated with 8.3 g. methyl iodide for one hour at 110°–120°, then again at 145°–155°. On opening the tube there was much pressure and a thick black oil resulted. This was extracted with ether and washed with sodium hydroxide. On evaporation, 2.5 g. of black oil was obtained which refused to solidify, and when heated began to boil at 100°; then the temperature rose to 250°, when the remaining material charred. Ethyl phenyl sulphone boils unaltered above 300°, and melts at 42°. Methyl phenylsulphone melts at 88°.

New Haven, May, 1899.

RESEARCHES ON SUBSTITUTION: THE ACTION OF BROMINE ON METACHLOR-, METABROM-, AND METAIODANILINES.*

[SECOND PAPER.]

By H. L. WHEELER and WILLIAM VALENTINE.

The action of meta-substituted anilines with chlorine and bromine has been thoroughly investigated only in regard to their behavior on saturation. In each case examined it has been found that the halogens enter the 2, 4, and 6 positions, the meta derivatives behaving, in this respect, precisely like aniline.

With this fact at hand, Langer † published the following law: "Dass bei weiterer Substitution des Anilins solche Substituenten, die zur Amido-gruppe die Metastellung einnehmen, gar keinen bemerkbaren Einfluss ausüben und die Zahl der neu eintretenden Halogenatome nicht verringern."

Previously Nölting, ‡ in calling attention to this similarity in behavior, stated: "Ueberhaupt verhält sich ein bei 3 substituirtes Anilin Agentien gegenüber gerade so wie ein gar nicht substituirtes."

These statements are perfectly true when applied in the sense indicated above, but it appears that, with the exception mentioned below, no attempts have been made to determine what the first product is, or what the chief products are when the free anilines are subjected to less energetic treatment. § Consequently it has not been shown in what order the differ-

* Amer. Chem. Jour., xxii, No. 4.

† Ann. Chem. (Liebig), ccxv, 107.

‡ Ber. d. chem. Ges., viii, 1098.

§ Beilstein and Kurbatow thoroughly investigated the action of chlorine on metachloracetanilide (Ann. Chem. (Liebig), cxcvi, 215), but do not mention the action of the free base.

ent positions 2, 4, and 6 are substituted, and whether or not in these intermediate stages any influence of the substituent in the meta position is to be observed.

Owing to the energy with which the aromatic amines are attacked by chlorine and bromine, and also on account of the formation of by-products, it is customary to moderate the action by employing the acetyl derivatives instead of the free bases. It has been assumed that this procedure simply protects the amino group or moderates the violence of the reaction. Whether in the case of meta-substituted anilines it exerts any other influence in the further substitution than this has not been determined, except in the instance described below. In the cases where the acetyl derivatives have been employed it has been found that the substitution takes place smoothly, the halogen entering the position para to the amino group and practically without the formation of by-products. In order to obtain the higher bromine substitution-products the free bases are employed, as, otherwise, the bromination is frequently arrested with the formation of the monobrom derivative, the next step being the formation of perhalides.*

Since the question whether a substituent in the meta position influences the further substitution of the aniline had been examined from only one side, one of us investigated the behavior of metanitraniline † with bromine, in glacial acetic acid, and found that the nitro group in the meta position exerts not only a protective or retarding influence ‡ but also a directing influence on the substitution. The chief product formed was the sweet-tasting 6-brom-3-nitraniline and not the expected 4-brom-3-nitraniline, which should result from analogy, or if the nitro group exerted no influence. Moreover, it was found that acetylmetanitraniline gave, as the chief product, a different mono derivative, 4-brom-3-nitraniline, than the free base.

We have now extended the examination of meta-substituted

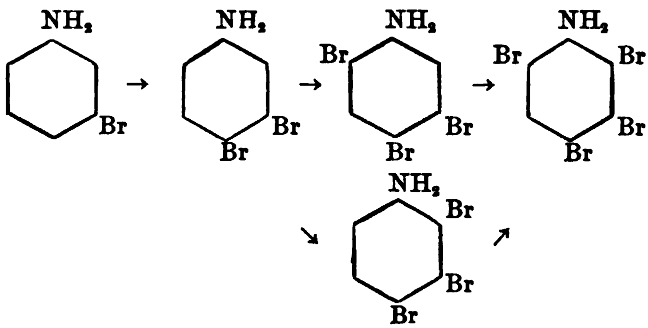
* Wheeler and Walden, Amer. Chem. Jour., xviii, 25; Wheeler, Barnes, and Pratt, Ibid., xix, 672.

† Ibid., xvii, 697.

‡ A fact previously noticed by Michael and Norton (Ber. d. chem. Ges., xi, 112), in the case of substitution by iodine monochloride.

anilines, and, in this paper, we describe the results of our experiments on the influence exerted when the meta substituent is a halogen, the bromination being conducted as before in a glacial acetic acid solution.*

Now, it might be expected that *m*-chlor-, *m*-brom-, and *m*-iodanilines would behave with bromine under similar conditions, like *m*-nitraniline. This, however, is not the case. The chief products formed in the case of the *m*-halogen anilines have been found to be the para derivatives. For example, in the case of *m*-bromaniline (43 g. with 1 molecular proportion of bromine) the product obtained in largest amount was 3,4-dibromaniline (26 g.); next in amount was a mixture of 3,4,6-tribromaniline (in larger amount) with 2,3,4-tribromaniline; then followed 2,3,4,6-tetrabromaniline, from which it follows that the relative tendency of bromine to substitute the hydrogen atoms in these compounds may be expressed in the terms 4>6>2, the course of the reaction proceeding as follows:



The bromination of metachlor- and metaiodaniline gave similar results, the bromine entering the para position to the amino group and forming chiefly a monobrom derivative.

* Glacial acetic acid has proved in each case to be well suited for the examination of the lower brominated products. It not only moderates the action less than the acetyl compounds, permitting the examination of the behavior of the free bases, but also simplifies the purification of the products.

Each of these cases is therefore an exception to the rule of Kehrmann,* *i. e.*, that the entering substituent generally takes the ortho position to the substituent of least molecular magnitude.

From the above it is seen that the nitro group in the meta position exerts a different directing influence on the further substitution by bromine than that exerted by the halogens; that the course of the reaction or the energy with which bromination occurs is in opposite directions around the molecules previous to the formation of the final 2,4,6-derivative.

It is well known that the nitro group in nitrobenzene exerts a different directing influence on further substitution from that exerted by the halogens in chlor-, brom-, and iodbenzene. Further substitution in the first case leads to the formation of meta derivatives, while in the latter ortho and para compounds result. The groups, atoms, or radicals that influence the entering substituent to take the ortho or para position have been termed by Lellmann † substituents of the *first class*. To this class belong the halogens, the alkyl radicals, and the groups $-NH_2$, $-OH$, $-CH_2R$, while the groups $-NO_2$, $-CO_2H$, $-SO_3H$, etc., which yield meta derivatives on further substitution, are known as substituents of the *second class*.

It is suggested by our work so far that a difference in directing influence is still retained by these radicals in the meta-substituted anilines. That, in general, meta-substituted anilines containing substituents of Lellmann's first class will be found to give chiefly a 4-halogen derivative, while, on the other hand, those with the radicals of the second class, like metanitraniline, will give a 6-halogen compound as the chief product. We intend to continue the investigation of the influence exerted on the substitution of anilines by groups in the meta position, and we hope, later, to decide the above simple questions, which, however, involve considerable work.

* Ber. d. chem. Ges., xxiii, 130.

† Principien d. Org. Synthese, p. 11.

The Bromination of m-Chloraniline.

When 50 g. of metachloraniline were dissolved in 400 c. c. of glacial acetic acid and treated with 62.7 g. of bromine (1 molecule) in the form of vapor, by means of a stream of dry air, a colorless crystalline precipitate separated. This, when dried, weighed 85 g. (precipitate *A*). It consisted mostly of the mono- and dibrom derivatives in the form of hydrobromic acid salts.* The monobrom derivative was extracted by treating this mixture repeatedly with water (solution *B*), and, on precipitating with ammonia, 35 g. of crude material were obtained.†

The treatment with water left the di- and a small amount of tribrom derivatives undissolved, weight 23 g. (residue *C*). The glacial acetic acid (solution *A*) was diluted with about three or four times its volume of water, which resulted in the precipitation of the rest of the tribrom derivative ‡ (1 g.) in practically pure condition (precipitate *D*).

The dilute acetic acid solution was then precipitated with strong ammonia, when the unaltered metachloraniline with some monobrom derivative was obtained (precipitate *E*). The method of examining and purifying these crude products is given below under their separate heads.

The following calculation, being a check on the above weights, confirms the analytical results and the chemical behavior of the products:

	Bromine. Grams.
B. 35 g. of monobrom derivative account for . .	27.1
C. 23 g. of dibrom derivative account for . . .	25.8
D. 1 g. of tribrom derivative accounts for . .	1.3
Total	54.2

That 8.5 g. of bromine are apparently not accounted for is due to the fact that the monobrom derivative mixed with un-

* It also contained the hydrobromic acid salt of unaltered material.

† A loss occurs here, owing to the solubility of the material in the solutions precipitated by ammonia. As this appeared to be chiefly unaltered material, it was not recovered.

‡ Some loss is to be expected here, owing to the volume of the solutions.

altered *m*-chloraniline (precipitate *E*) is not included in the above calculation, and also to the fact that the above are weights of crude products and not of perfectly pure material.

It is to be expected that the loss in the case of metachloraniline would be greater than with metabromaniline, since the chlorine compounds are more soluble. This has been found to be the case, so that the solubility explains a part of this loss. The amount of bromine lost by action on the glacial acetic acid is probably very small. Each one of the brominations described in this paper has been repeated and the results confirmed.

3-Chlor-4-bromaniline. — The precipitate produced by ammonia in solution *B* was crystallized from dilute alcohol, when four- and six-sided colorless plates separated. They melted constantly from 67° to 68°, and a determination of the halogens shows that this material is a monobrom derivative:

	Calculated for C_6H_5NClBr.	Found.
Cl	17.2	17.2
Br	38.7	38.2

The structure is shown by the fact that it gives orthochlorbrombenzene with ethyl nitrite, and since it is formed almost quantitatively by brominating acetyl-*m*-chloraniline, the bromine as usual taking the position para to the acetyl group.

The *hydrochloride*, prepared by passing hydrochloric acid gas into the alcoholic solution of the base, crystallizes in colorless needles. A hydrochloric acid determination gave:

	Calculated for $C_6H_5NClBr.HCl$.	Found.
HCl	15.0	14.6

It is readily soluble in water, less readily in alcohol, and insoluble in benzene. It blackens when heated to about 210°.

The *sulphate* is obtained in the form of colorless plates when the base is treated with dilute sulphuric acid. A sulphuric acid determination gave:

	Calculated for $(C_6H_5NClBr)_2H_2SO_4$.	Found.
H_2SO_4	19.2	19.5

The *picrate* is obtained as a precipitate by adding an alcoholic solution of picric acid to a solution of the base. It crystallizes in yellow needles which melt at 141°. A nitrogen determination gave the following result:

	Calculated for $C_6H_5NClBr.C_6H_3N_3O_7$.	Found.
N	12.9	12.7

1,2-Chlorbrombenzene. — 6 g. of the precipitate produced by ammonia in solution *B* were treated with an excess of ethyl nitrite in the presence of a little concentrated hydrochloric acid. After warming, the material was taken up in ether, washed, dried, and distilled, when 4.5 g. of colorless oil were obtained, boiling from 200° to 210°. On redistilling at 772 mm. pressure it all boiled from 201° to 204°. It refused to solidify. *p*-Chlorbrombenzene is a solid melting at 67.4°, while the boiling-points of ortho-, meta-, and parachlorbrombenzene are given by Dobbie and Marsden * at 204°, 196°, and 196.3°, respectively. Our material is therefore orthochlorbrombenzene.

Nitration of 1,2-Chlorbrombenzene. — In order further to characterize orthochlorbrombenzene we have examined its behavior towards nitric acid. 2 to 3 g. of orthochlorbrombenzene were dissolved in fuming nitric acid and warmed. Water was then added, and the precipitated material, crystallized from 75 per cent alcohol, gave colorless needles melting from 49° to 50°. Three crystallizations did not alter the melting-point.† A nitrogen determination gave:

	Calculated for $C_6H_3NO_2ClBr$.	Found.
N	5.9	6.3

The structure $C_6H_3NO_2ClBr$,1,4,3, is assigned to this compound, because on reduction it did not give 3-chlor-4-bromaniline, melting at 67°, but a base melting at 75°, after repeated crystallizations. Since, in general, the tendency of

* J. Chem. Soc., 1898, 255.

† The true melting-point of 3-brom-4-chlornitrobenzene is probably 60°, the above material being mixed with some 3-chlor-4-bromnitrobenzene.

ortho compounds, on nitration, is to form an unsymmetrical in preference to a vicinal derivative, it follows that this is in all probability *4-chlor-3-bromaniline.* It was not further examined.

3-Chlor-4-brom-2,6-dinitraniline. — 8 g. of 3-chlor-4-bromaniline were heated on the steam-bath with concentrated nitric acid. In a few minutes reaction set in with evolution of red fumes. After this was over the solution was diluted with water and the precipitate crystallized from absolute alcohol, in which it is difficultly soluble, when it was obtained in the form of dark-yellow prisms, melting from 169° to 170°. A nitrogen determination gave:

	Calculated for $C_6H_3N_3O_4ClBr$.	Found.
N	14.2	14.7

3-Chlor-4-bromacetanilide. — 50 g. of metachloracetanilide were dissolved in glacial acetic acid, the calculated quantity of bromine was added, and the mixture allowed to stand a few minutes. Water was then added, and the precipitate was crystallized from 50 per cent acetic acid, when it was found to melt sharply at 125°; yield 70 g., calculated 73 g. A nitrogen determination gave:

	Calculated for $C_8H_7NOClBr$.	Found.
N	5.6	5.7

The acetyl group is easily removed from this by boiling the alcoholic solution with a little concentrated hydrochloric acid. This gives the hydrochloride of a base which latter is identical in every respect with the monobrom compound formed on brominating *m*-chloraniline.

3-Chlor-4-brom-6-nitroacetanilide. — One part of 3-chlor-4-bromacetanilide is dissolved in 3 parts of cold nitric acid (sp. gr. 1.52) and the solution is allowed to stand for a few minutes. It is then poured into ice-water, and the precipitate, crystallized from absolute alcohol, gives colorless, flattened prisms or plates. These melt from 129° to 130°. Yield 7 g. from 5 g. acetyl compound. A nitrogen determination gave:

	Calculated for $C_8H_6N_2O_3ClBr$.	Found.
N	9.5	9.3

3-Chlor-4-brom-6-nitraniline. — 5 g. of the above substance were boiled with alcohol containing some concentrated hydrochloric acid, when crystalline material began to separate. Water then precipitated the base completely, ammonia giving no precipitate in the filtrate, as the substance is too weakly basic to form a salt under these conditions. It crystallizes from alcohol in long yellow needle-like prisms which melt from 202° to 203°. A nitrogen determination gave:

	Calculated for $C_6H_4N_2O_2ClBr$.	Found.
N	11.1	11.0

4-Chlor-3-bromnitrobenzene. — From 2 to 3 g. of the above compound were treated with nitrous acid in alcohol. The material after this treatment was crystallized from alcohol, when light-yellow needles melting at 60° were obtained.

4-Chlor-3-bromaniline. — On reducing the above 4-chlor-3-bromnitrobenzene with tin and hydrochloric acid, a product identical with the base obtained from the nitration of 1,2-chlorbrombenzene should result. This being the case, the structure of this and the four preceding compounds is proved. In fact, a base was obtained which appears to be identical with that described under the head of the nitration of 1,2-chlorbrombenzene. The crude product melted at 75°, but on further crystallizing it was obtained in the form of colorless, shining plates, which melted at 78°. A nitrogen determination gave:

	Calculated for C_6H_5NClBr.	Found.
N	6.8	6.5

3-Chlor-4,6-dibromaniline. — Residue *B* (see above), after being treated thoroughly with water, was crystallized from alcohol, when thin, colorless plates were obtained, melting from 79° to 80°. A halogen determination gave:

	Calculated for $C_6H_4NClBr_2$	Found.
Cl	12.4	12.4
Br	56.0	55.9

3-Chlor-2,4,6-tribromaniline. — On crystallizing precipitate *C* (see above) from alcohol this compound was obtained. It had all the properties described by Langer.*

The Bromination of m-Bromaniline.

In one experiment 43 g. of metabromaniline were dissolved in 350 c. c. of glacial acetic acid, and 40 g. of bromine (1 molecule) added as described in the previous case. The precipitate produced (*A*) weighed 90 g. The soluble hydrobromides removed by water and precipitated by ammonia (*B*) weighed 26 g. The residue (*C*) weighed 16 g. The precipitate (*D*) produced by water in the glacial acid solution weighed 1 g., and on filtering from this and adding ammonia practically nothing but unaltered material was found.

The results are checked by the following calculation:

	Bromine. Grams.
B. 26 g. of dibrom derivative account for . . .	17.7
C. 16 g. of tribrom derivative account for . . .	15.5
D. 1 g. of tetrabrom derivative accounts for .	1.1
Total	34.3

This gives 5.7 g. of bromine not accounted for. It is to be explained in the same manner as the loss in the case of the previous bromination.

3,4-Dibromaniline. — The precipitate by ammonia (*B*), after two crystallizations from 50 per cent alcohol, melted from 80° to 81°. It had all the properties of the base produced by reducing 3,4-dibromnitrobenzene.†

The *picrate* was obtained by mixing alcoholic solutions of the constituents. The product crystallized from water gave yellow needles, melting at 149°. A nitrogen determination gave:

* Loc. cit.

† Körner, Jahresb., 1875, 311.

	Calculated for $C_6H_5NBr_2.C_6H_3N_3O_7$.	Found.
N	11.66	11.7

The *hydrochloride* crystallizes from dilute hydrochloric acid in colorless prisms which decompose when heated from 220° to 230°. A hydrochloric acid determination gave:

	Calculated for $C_6H_5NBr_2.HCl$.	Found.
HCl	12.7	12.7

The *sulphate* crystallizes in colorless plates.

	Calculated for $(C_6H_5NBr_2)_2.H_2SO_4$.	Found.
H_2SO_4	16.3	16.5

3,4-Dibromacetanilide. — This has recently been prepared * by brominating metabromacetanilide. We have prepared it in this way, and also by acetylating precipitate *B*. It crystallizes in slender prisms melting at 128°, as stated by Körner.

3,4,6-Tribromaniline. — When residue *C* (see above) was crystallized from alcohol, colorless needles were obtained which melted from 115° to 116°. This proved to be 2,3,4,6-tetrabromaniline. In order to separate this from the tribromanilines the material was taken up in dry ether and hydrochloric acid gas passed in. This produced a precipitate of the hydrochloric acid salts of the tribromanilines, while the tetrabromaniline remained in solution. The precipitate was treated with ammonia and repeatedly crystallized from alcohol, when it melted from 84° to 89°. It being still impure, it was converted into the acetyl compound. This, on repeated crystallization from alcohol, melted at 188°–189°; on now removing the acetyl group, the free base melted sharply at 85°–86°. A bromine determination in the product melting at 84°–89° gave:

	Calculated for $C_6H_4NBr_3$.	Found.
Br	72.7	72.2

* Körner, Bull. Soc. Chim. (Paris), 1896, 1047.

1,3,4-Tribrombenzene. — In order to determine the structure of the above tribromaniline, 1 g. was treated with nitrous acid in alcoholic solution, when a small amount of fine, colorless needles were obtained; these melted from 44° to 45°, and were undoubtedly 1,3,4-tribrombenzene, which forms needles and melts at 44°. The above base, melting at 85°–86°, is, therefore, 3,4,6-tribromaniline.

3,4,6-Tribromacetanilide is therefore the compound crystallizing in colorless needles and melting from 188° to 189°, as mentioned above. This same compound and the corresponding base were also prepared in the following manner: *p*-Dibrombenzene was nitrated and the product reduced; this gave 3,6-dibromaniline, which melted from 51° to 52°, and agreed in properties with Meyer and Stüber's * description, except that, when sufficiently purified, it does not have the odor of *a*-naphthylamine. On acetylating, 3,6-dibromacetanilide was obtained.

3,6-Dibromacetanilide, on crystallizing from alcohol, was found to melt from 171° to 172°, and a nitrogen determination gave:

	Calculated for $C_8H_7NOBr_2$.	Found.
N	4.8	4.8

3,4,6-Tribromacetanilide. — The above acetyl compound was dissolved in glacial acetic acid and treated with 1 molecular proportion of bromine, when a product was obtained which crystallized from alcohol in colorless needles and melted from 188° to 189°. This is identical in every respect with the acetyl compound obtained from residue *C*. A nitrogen determination gave:

	Calculated for $C_8H_6NOBr_3$.	Found.
N	3.9	3.8

Here again the different influence of groups in the meta position is to be noticed. The above 3,6-dibromacetanilide is readily attacked by bromine, while 3-nitro-6-bromacetanilide can be crystallized unaltered from pure bromine.

* Ann. Chem. (Liebig), clxv, 180.

1,2,3-Tribrombenzene. — In another experiment the crude product, *C*, after removal of 2,3,4,6-tetrabrombenzene, was treated directly with nitrous acid, in alcohol, in the presence of hydrochloric acid.* On distilling with steam an oil was obtained which, after solidification and crystallization from alcohol, was obtained in the form of colorless plates. These had the odor of the brombenzenes and melted at 85°. Körner † gives the melting-point of 1,2,3-tribrombenzene as 87.4°.

It follows, therefore, that the residue *C* consists of 3,4,6-tribromaniline (isolated), 2,3,4-tribromaniline (not isolated), and 2,3,4,6-tetrabromaniline (isolated).

2,3,4,6-Tetrabrombenzene. — The precipitate *D* was found to consist entirely of this. It forms colorless needles, melting from 115° to 116°, as described by Körner. ‡

The Bromination of m-Iodaniline.

In one experiment 53 g. of *m*-iodaniline were dissolved in 400 c. c. of glacial acetic acid, and 39 g. of bromine were added in the form of vapor. This produced a crystalline precipitate weighing 83 g. (*A*). The material obtained by extracting this with water and precipitating with ammonia (precipitate *B*) weighed 35 g. The residue *C* weighed 30 g., and the precipitate *D*, produced by water in the glacial acetic acid solution, weighed 1 g. Ammonia added to the filtrate from this gave unaltered material. Checking these weights now by the following calculation, we find that:

		Bromine. Grams.
B.	35 g. of monobrom derivative account for . .	18.7
C.	30 g. of dibrom derivative account for . . .	25.4
D.	1 g. of tribrom derivative accounts for . .	1.0
	Total	45.1

* These tribromanilines have a great tendency to form orange-colored precipitates (diazoamidobenzenes?) which are decomposed with difficulty by nitrous acid.

† Gazz. chim. ital., iv, 408.

‡ Loc. cit.

This gives an excess of 6.1 g. of bromine. The error lies chiefly in the assumption that *B* consists entirely of monobrom derivative. As it was not free from oil, it must have contained unaltered material which, calculated as monobrom derivative, explains this excess.

3-Iod-4-bromaniline. — Precipitate *B* was crystallized from alcohol, when it was obtained in the form of colorless plates, melting at 77°. A bromine and iodine determination gave the following:

	Calculated for C_6H_5NBrI.	Found.
Br	26.8	27.3
I	42.6	42.3

We proved the structure of this compound in the following manner: 2.5 g. of 6-brom-3-nitraniline (which gives *p*-bromnitrobenzene with ethyl nitrite) were diazotized, and the amino group replaced by iodine by means of potassium iodide. The *3-iod-4-bromnitrobenzene* thus produced crystallized from alcohol in four- and six-sided tables, which melt at 95°–96°, and on reduction the material gave a base melting at 77° and having all the properties of the compound obtained by brominating *m*-iodaniline.

The *hydrochloride* was made by passing hydrogen chloride into the benzene solution of the base. It crystallizes from alcohol in long, slender, colorless needles, which decompose when heated at about 210°. A determination of the hydrochloric acid gave:

	Calculated for $C_6H_5NBrI.HCl$.	Found.
HCl	10.9	10.6

The *sulphate* crystallizes in colorless plates from dilute sulphuric acid.

	Calculated for $(C_6H_5NBrI)_2.H_2SO_4$.	Found.
H_2SO_4	14.1	14.2

The *picrate* crystallizes from water in yellow needles, which melt from 158° to 159°. A nitrogen determination gave:

	Calculated for $C_6H_5NBrI.C_6H_3N_3O_7$.	Found.
N	10.6	10.9

3-Iod-4-bromacetanilide was prepared by acetylating the above base in the usual way. On crystallizing from alcohol it melted from 138° to 139°. A nitrogen determination gave:

	Calculated for C_8H_7NOBrI.	Found.
N	4.1	4.2

3-Iod-4,6-dibromaniline. — The residue *C*, which was insoluble in water, on repeated crystallizations from alcohol, separated in the form of long, colorless prisms, melting at 81°. A bromine and iodine determination gave:

	Calculated for $C_6H_4NBr_2I$.	Found.
Br	42.4	42.6
I.	33.7	33.6

3-Iod-2,4,6-tribromaniline. — The precipitate *D*, produced by adding water to the glacial acetic acid solution, was crystallized from alcohol, when minute colorless prisms or plates were obtained, melting at 115°–116°. A bromine and iodine determination gave:

	Calculated for $C_6H_3NBr_3I$.	Found.
Br	52.6	52.3
I.	27.8	27.8

New Haven, June, 1899.

ON THE REARRANGEMENT OF IMIDO-ESTERS.[*]

[SECOND PAPER.]

By HENRY L. WHEELER.

As described in our[†] first paper on this subject, we had occasion to prepare phenylformimidoethyl ester, and, instead of following the usual method[‡] of treating silver formanilide with ethyl iodide at low temperatures, we heated the materials in a closed tube to 100°. We thereupon unexpectedly obtained a rearrangement of phenylformimidoethyl ester into the isomeric ethyl anilide:[§]

$$HC\begin{matrix}\diagup\!\!\diagup NC_6H_5\\ \diagdown OAg\end{matrix} \rightarrow HC\begin{matrix}\diagup\!\!\diagup NC_6H_5\\ \diagdown OC_2H_5\end{matrix} \rightarrow HC\begin{matrix}\diagup N<\begin{matrix}C_6H_5\\ C_2H_5\end{matrix}\\ \diagdown\!\!\diagdown O\end{matrix}.$$

This was confirmed by the fact that benzimidoethyl ester gave ethylbenzamide when heated with ethyl iodide. We stated that we hoped to reserve the further examination of this rearrangement for this laboratory.

On the publication of these results Professor Knorr called our attention to his work along similar lines in the case of the cycloimido esters. He had previously shown that the oxygen esters of the α-quinolones[‖] are converted by methyl iodide

* Amer. Chem. Jour., xxiii, No. 2.

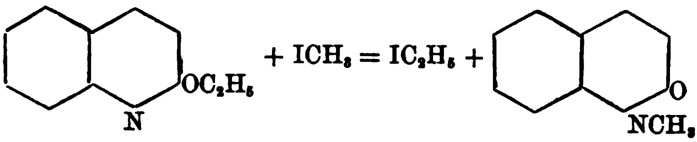
† Wheeler and Johnson, Amer. Chem. Jour., xxi, 185.

‡ Comstock, Amer. Chem. Jour., xiii, 514.

§ The prediction of Freer and Sherman in regard to this salt is now completely fulfilled, *i. e.*, "With suitable alkyl or acyl halides and alteration of conditions, it will probably be possible to procure both oxy and nitrogen derivatives from the silver salt." (Amer. Chem. Jour., xviii, 571.) In Amer. Chem. Jour., xviii, 381, Wheeler and Boltwood showed that this salt gives in fact benzoylformanilide, a nitrogen derivative, with benzoyl chloride.

‖ Ber. d. chem. Ges., xxx, 929.

"langsam schon in der Kälte, rasch und vollständig in der Wärme, in die Stickstoff-Methylester." Thus, ethoxyquinoline is converted into methylquinolone:



He also found that the oxygen methyl and ethyl esters of oxy-γ-lepidine behaved in a similar manner. He showed that this reaction in the case of γ-methoxyquinaldine * takes place first by addition; and that this intermediate product then when heated to 200° gives the nitrogen derivative. Again, along with E. Fertig,† he found that α-phenyl-γ-methoxyquinoline was converted directly into the isomeric derivative with methyl iodide, and finally he stated: "Ich hoffe bald weitere Mittheilung machen zu können, ob sich ganz allgemein die Imidoäther R′N : CR″OR‴ durch Jodmethyl in Amide secundärer Basen, CH_3R′NCR″O überführen lassen."

In view, however, of the work already done in this laboratory, and, since I informed Professor Knorr of my desire to publish the work of my students, which was finished at the time our first publication appeared, Professor Knorr kindly gave over the entire field to me.

I wish to take advantage of this occasion to thank him for his kindness and also to refer to other work bearing on the rearrangement of the imido-esters.

In the year 1885 Ponomarew ‡ found that by treating silver cyanurate with alkyl iodides, at low temperatures, the oxygen esters result, while at higher temperatures the nitrogen esters are the chief products.

In 1886 Hofmann § showed that the oxygen methyl ester of cyanuric acid is transformed into the nitrogen ester simply by heating.

* Ber. d. chem. Ges., xxx, 924, 926.
† Ibid., xxx, 937.
‡ Ibid., xviii, 3271.
§ Ibid., xix, 2061.

In 1891 Andreocci * found that when phenylpyrodiazolon or phenylmethylpyrodiazolon is methylated, and then treated with methyl iodide, similar results are obtained, and that the oxygen methyl compounds, when heated to 200°, are also transformed into the nitrogen compounds.

All the above are examples of the rearrangement of cycloimido esters. The transformation of benzimidochlorethyl ester into β-chlorethylbenzamide, under the influence of heat alone, as described by Gabriel and Neumann, † is especially interesting, and, outside of our work, this appears to be the only known example of a rearrangement taking place in the acyclic series.‡

In the cycloimido ester series N-alkyl derivatives have frequently been obtained from silver salts, but particularly at higher temperatures. This has notably been the case in the uric acid group in Fischer's investigations.§ Since, however, the silver salt of hydroxycaffeïn gives with ethyl iodide chiefly ethoxycaffeïn, he concludes that the former substance does not have the grouping –CO–NH, but –COH=N–. In this case he also noticed the formation of some tetramethyluric acid.

We find that the imido-esters of Pinner react slowly, even at ordinary temperatures with methyl and ethyl iodides giving alkyl amides. In the case of the benzimido-esters benzamide and benzonitril invariably accompany the alkyl amide. In the lower-boiling portions of the reaction-product the presence, in small amount, of a substance that gave off an amine odor on distilling was also observed.

With isobutyl iodide the chief products were benzamide and isobutylene:

* Ber. d. chem. Ges., xxiv, R, 203. † Ibid., xxv, 2383.

‡ I wish to express my thanks to Professor Gabriel for calling my attention to this work. In a private communication from Dr. Stieglitz the following was mentioned: "I intended calling your attention to Knorr's paper in the Berichte, 1897, pp. 929–933. At the time when this came out I was heating ethyl imidobenzoate in a sealed tube at 100° with ethyl iodide, but did not go on with the action on account of Knorr's reservation."

§ Ber. d. chem. Ges., xxx, 550.

$$C_4H_9I = C_4H_8 + HI,$$

and $$C_6H_5C(NH)OC_4H_9 + HI = C_6H_5CO.NH_2 + C_4H_9I.$$

In general, however, the chief reaction of methyl and ethyl iodides is as follows:

$$C_6H_5C\left\langle\begin{matrix}NH\\OC_4H_9\end{matrix}\right. + CH_3I = C_6H_5C\left\langle\begin{matrix}NHCH_3\\O\end{matrix}\right. + C_4H_9I.$$

In the case of the action of ethyl iodide on benzimidoethyl ester, diethylbenzamide was sought for, but no evidence of its presence was observed.

Besides others there are, therefore, three principal reactions that take place when the acyclic imido-esters are treated with the lower alkyl iodides:

a. A transference of alkyl group from oxygen to nitrogen.

b. The formation of hydrogen iodide which with unaltered imido-ester gives a primary amide (benzamide).

c. A decomposition of the imido-ester into nitril and alcohol.

*Experiments with Benzimido-esters.**

Benzimidomethylester and methyl iodide readily react at ordinary temperature. 30 g. of the imido-ester were allowed to stand for a month with 16 g. of methyl iodide (0.5 molecule); in a short time crystals separated, which finally developed into well-crystallized, flattened prisms. This material proved to be benzamide containing a small amount of cyanphenin, and it weighed 3.5 g. The oil filtered from this was distilled at 13–12 mm. pressure (*A* below).

For comparison, 20 g. of the ester were heated to about 100° for five and a half hours with 1 g. of methyl iodide. On cooling, crystals separated but were not filtered off, the whole being distilled at 9–12 mm. pressure, when the following fractions were obtained (*B*):

* The imido-esters in the following experiments were all freshly distilled. Under diminished pressure they boil unaltered without exception.

A.	G.	B.	G.
(1) below 159°	3.4	(1) below 155°	2.9
(2) 159°–169°	9.8	(2) 155°–165°	7.9
(3) 169°–174°	11.5	(3) 165°–168°	7.7

The first portions, in both cases, consisted chiefly of benzonitril.

The second portions did not solidify on standing or when cooled in a freezing-mixture. When distilled at 760 mm. pressure, *B* (2), for example, began to boil at 276°, and a strong odor of amine and benzonitril was given off. The material had no constant boiling-point, but distilled steadily up to 291°, when the distillation was stopped and the residue (the greater portion) was cooled. It then solidified and, when crystallized from a small amount of alcohol, gave colorless flattened prisms melting at 82°. This material had all the properties of methylbenzamide (see below).

The third fractions in both cases readily solidified and were crystallized from water. *A* (3) gave square tables of methylbenzamide, while *B* (3), from which benzamide was not removed by filtration, gave a mass of plates melting at 128°, *i. e.*, benzamide.*

The products identified in these reactions are, therefore, methylbenzamide, benzamide, benzonitril, and a trace of cyanphenin.

From the above it appears that the action of methyl iodide on benzimidomethyl ester is the same at 100° as at ordinary temperatures, and that a small amount of methyl iodide produces practically the same result in this reaction as a large amount.

Benzimidoethyl Ester and Ethyl Iodide. — In the previous

* In describing benzimidomethyl ester (Amer. Chem. Jour., xvii, 398), the author stated that this ester, on standing, deposits benzamide. It is now known that this result was due to the presence of methyl iodide, since the pure ester prepared by Pinner's method does not deposit benzamide on standing. Dains (J. Am. Chem. Soc., xxi, 166), in his work on the isoureas, quotes this supposed behavior in his comparisons. Benzimidomethyl ester, when pure, is quite stable.

paper the ester was heated with ethyl iodide, while the following is a description of the action at ordinary temperatures: 49 g. of the ester were mixed with 52 g. of ethyl iodide and allowed to stand for a month. At the end of this time 5.2 g. of beautifully crystallized cyanphenin separated. It melted sharply from 230° to 231°. The filtrate from this was distilled at 773 mm. pressure, when 51.7 g. of crude ethyl iodide were recovered (below 185°). After the ethyl iodide was over, the material began to distil at 185°, when, up to 278°, 2 g. of fishy-smelling oil were obtained, mostly benzonitril. From 278° to 293° 10.8 g. of oil were collected, while from 293° to 300° the remainder practically all came over. This weighed 23.5 g. and when crystallized once from dilute alcohol it separated in small flattened prisms and melted from 69° to 70°, this material being pure ethylbenzamide.

A search was made for diethylbenzamide in the portion boiling from 278° to 293°, it having been found that this substance boils at 282°. For this purpose the fraction was cooled in a freezing-mixture, and considerable ethylbenzamide was then removed by filtering. The filtrate, when distilled at 763 mm. pressure, gave a few drops of fishy-smelling oil below 200°; then up to 290° no definite boiling-point was observed, the mercury in the thermometer not stopping an instant at the boiling-point of diethylbenzamide. From the lower-boiling portion of this fraction benzonitril was obtained; the higher consisted mostly of benzamide.

The chief products of this reaction are, therefore, ethylbenzamide, benzamide, benzonitril, and cyanphenin.

Diethylbenzamide was prepared from 5 g. of diethylamine by means of the Baumann-Schotten reaction. It was obtained as a clear, colorless oil that became thick, but did not solidify at –25°. It boiled from 282° to 283° at 763 mm. pressure, and agreed in properties with the products obtained by Hallmann* and by Romburgh.† It is less soluble in warm water than in cold.

* Ber. d. chem. Ges., ix, 846.

† Recueil d. Travaux chim. d. Pays-Bas., iv, 387.

An experiment to determine whether benzonitril, ethyl iodide, and ethyl alcohol react under the above conditions was performed as follows: 10.5 g. of benzonitril were mixed with alcohol and ethyl iodide in molecular proportions and the mixture heated from 100° to 115° for nine hours. On opening the tube there was no pressure, and, on distilling at about 10 mm. pressure, the entire material boiled from 71° to 72° (benzonitril), except a few drops of black tar which remained in the residue. No benzamide or ethylbenzamide was formed.

Benzimidoisobutyl Ester and Methyl Iodide. — 30 g. of the ester were heated with a little over one molecular proportion of methyl iodide from 80° to 115° for four hours. On cooling, an oil was obtained containing some crystals in suspension. They were filtered and consisted of cyanphenin and benzamide (separated by boiling water). The oil was distilled at 765 mm. pressure, when the portion boiling below 160° was collected. It weighed 24 g., while the calculated yield of isobutyl iodide is 31 g. On redistilling, it boiled mostly from 121° to 121.5°, and proved to be pure isobutyl iodide.

The residue boiling above 160° was then distilled at 18–19 mm. pressure, when three fractions were obtained: (1) 98°–172° (benzonitril); (2) 172°–177°; (3) 177°–187°. The last portion readily solidified; the second deposited crystals on standing. On crystallizing the material from alcohol, prisms were obtained melting at 82°. Romburgh gives 78° as the melting-point of methylbenzamide. That the material is methylbenzamide is shown by its properties and the following nitrogen determination:

	Calculated for C_8H_9NO.	Found.
N	10.37	10.40

The most striking property of the alkylbenzamides is the behavior of their saturated aqueous solutions. When these are warmed they become turbid in consequence of the separation of the amides in the form of oils. This turbidity dis-

appears again on warming to boiling, and on again cooling, this behavior is reversed.

Benzimidoisobutyl Ester and Isobutyl Iodide. — 30 g. of the former were heated from 165° to 185° for several hours. On cooling and opening the tube considerable inflammable gas escaped. It was concluded from its odor that this was isobutylene. On distilling, 21 g. of isobutyl iodide were recovered. The remaining material was distilled at 13 mm. pressure, when benzonitril and benzamide were the chief products. The higher-boiling portion was crystallized from water, when it melted from 126° to 127°, and a nitrogen determination gave:

	Calculated for $C_6H_5CO.NH_2$.	Found.
N	11.57	11.22

Isobutylbenzamide. — This was prepared from 6 g. of isobutylamine by the Baumann-Schotten method. The material thus prepared boiled from 173° to 178° at 13 mm. pressure, and at 308°–318°, with slight decomposition, at 760 mm. pressure. The oil thus obtained solidified to a beautiful crystalline mass, which was crystallized from alcohol with the aid of a freezing-mixture. It then melted at from 57° to 58°. A nitrogen determination gave:

	Calculated for $C_{11}H_{15}NO$.	Found.
N	7.91	8.19

Isobutylbenzamide forms chisel-shaped prisms, and is difficultly soluble in water and petroleum ether, readily in ether, chloroform, and alcohol.

Benzimidoethyl ester and isobutyl iodide did not act smoothly. The products obtained were benzamide, benzonitril, cyanphenin, ethyl and isobutyl benzamides, and a substance, in too small amount for identification, which, after crystallization from alcohol separated in colorless, stout crystals, which melted at 192° with effervescence.

Experiments with Phenylacetimido-esters.

By TREAT B. JOHNSON.

Phenylacetimidomethyl Ester and Methyl Iodide. — (1) 20 g. of phenylacetimidomethyl ester were heated with 9.5 g. of methyl iodide (1 molecule of ester to 0.5 molecule of iodide) for an hour from 95° to 105°. The product was then diluted with ether and the precipitated material filtered off. This proved to be phenylacetamide, and weighed 2.2 g. The ether solution was evaporated and the oil distilled at 25–28 mm. pressure. The first fraction was collected from 115° to 187°. This weighed 4.2 g. and consisted mostly of phenylacetonitril. The second fraction was collected from 187° to 197°. This weighed 6 g., and was crude methylphenylacetamide containing phenylacetamide. On crystallizing it from benzene and ligroïn it melted at 147°, and on recrystallizing it from water it melted from 154° to 155° (the melting-point of phenylacetamide). If, however, the higher-boiling fractions are crystallized from alcohol by means of a freezing-mixture, methylphenylacetamide is obtained.

(2) For comparison, 20 g. of phenylacetimidomethyl ester were again heated, this time with only 0.6 g. of methyl iodide for six hours to the same temperature as before. The residue left by ether (phenylacetamide) weighed 2.7 g. On distilling the remainder at 27 mm. pressure the first fraction, boiling between 110° and 187°, weighed 4.8 g.; the second fraction, 187°–197°, weighed 5.5 g.

(3) In another experiment 30 g. of the ester were heated with 14.2 g. of methyl iodide, for six hours, from 100° to 110°. In this case the phenylacetamide weighed 3.6 g. The first fraction of the oil distilled at about 20 mm. pressure, boiled at from 110° to 180° (mostly 110°–130°), and weighed 8.4 g.; the second fraction (184°–190° at 18 mm. pressure) weighed 10.5 g. This latter was combined with the second fraction obtained in our second experiment and redistilled at 19 mm. pressure, when the greater portion boiled from 179° to 184°,

leaving little or no residue. This distillate readily solidified, and, when crystallized from alcohol, finally melted from 54° to 57° (the melting-point of methylphenylacetamide is given by Taverne * as 58°).

A nitrogen determination in this material gave:

	Calculated for $C_6H_5CH_2CONHCH_3$.	Found.
N	9.39	9.14

The substance formed in chief amount in these reactions is, therefore, methylphenylacetamide.

In order to simplify the comparison, the above results are given in the following table:

	Weight of Ester taken.	Weight of Iodide.	Time.	Weight of Phenyl-acetamide. (*b*)	Weight of First Fractions. Crude Nitril. (*c*)	Weight of Second Fractions. Crude Methyl Amide. (*a*)
(1)	20	9.5	1 hr.	2.2	4.2	6.0
(2)	20	0.6	6 hrs.	2.7	4.8	5.5
(3)	30	14.2	6 hrs.	3.6	8.4	10.5

From this it is evident that in this rearrangement the same result is obtained whether a little (0.6 g.) or a large amount (9.5 g.) of alkyl iodide is used. The close agreement of experiments (1) and (2) under widely different conditions suggests that there is some definite relation between the three principal reactions mentioned in the introduction. The columns (*a*, *b*, *c*) show roughly to what extent these three reactions take place. In estimating this, however, it must be remembered that the total weight of phenylacetamide is low according to column (*b*); that the weight of nitril includes some phenyl- and some methylphenylacetamide; and that column (*a*) represents a mixture of the latter two substances.

Phenylacetimidoethyl Ester and Ethyl Iodide. — 20 g. of the ester were heated at 100°–106° with 19.1 g. of iodide for six hours. On cooling, the tube contained a thick red oil, together with some plates. The contents of the tube were extracted with ether, and the insoluble residue, after being

* Recueil d. Travaux chim. d. Pays-Bas., xvi, 35.

crystallized from water, melted from 153° to 154°; this was pure phenylacetamide. The ether was then evaporated and the remaining oil was distilled at 13 mm. pressure. The first fraction, collected below 178°, proved to be chiefly phenylacetonitril. The second fraction, collected from 188° to 198° at 17 mm. pressure, was obtained as a thick oil which soon solidified in a freezing-mixture. This, when crystallized twice from water, separated in the form of colorless plates melting from 73° to 74°. A nitrogen determination shows that this material is ethylphenylacetamide:

	Calculated for $C_6H_5CH_2CONHC_2H_5$.	Found.
N	8.58	8.45

In this rearrangement, in certain cases, some high-boiling material was formed, but this decomposition-product was not examined.

(2) 34.8 g. of phenylacetimidoethyl ester were heated with 33.3 g. of ethyl iodide (1 molecule of ester to 1 molecule of iodide) for six hours from 95° to 106°. The amount of phenylacetamide then obtained, on proceeding as above, weighed 2.5 g., and the amount of crude ethylphenylacetamide weighed 10.9 g., the remainder being phenylacetonitril and some high-boiling residue.

(3) In another experiment 20 g. of the ester were heated to 100°–110° for six hours with 19.1 g. of ethyl iodide, when the amount of amide isolated weighed 1.3 g., and the amount of crude ethylamide weighed 5.2 g.

In all of the above experiments the first fractions were tested for unaltered imido-ester by mixing a portion with benzene, and passing in dry hydrogen chloride, when no precipitate was produced; hence in each case the imido-ester had entered into reaction completely.

Experiments with Furimidomethyl Ester, *p*-Tolenylimidomethyl Ester, and β-Naphthylimidoethyl Ester.

By MUNSON D. ATWATER.

Furimidomethyl Ester, $C_4H_3O.C\begin{smallmatrix}\diagup NH \\ \diagdown OCH_3\end{smallmatrix}$, was easily obtained from furyl cyanide by following the directions of Pinner * for the preparation of the corresponding ethyl ester. It was obtained as a clear, colorless oil of peculiar odor. When distilled at 8 mm. pressure, it boiled from 52° to 57°. Redistilled at 762 mm. pressure, it boiled from 169° to 172°; and a nitrogen determination gave the following result:

	Calculated for $C_6H_7NO_2$.	Found.
N	11.2	11.4

Furimidomethyl Ester and Methyl Iodide. — (1) 19 g. of the ester were heated for six hours at 100° with a little over 10 g. of methyl iodide. The product, a light-yellow oil, was distilled at 21 mm. pressure, when 12 g. of material boiling from 137° to 147°, was obtained. This was redistilled at ordinary pressure and collected between 250° and 253°. This portion, on standing several days in a desiccator, deposited a considerable crop of colorless, stout crystals, which, when crystallized from ligroïn, melted at 64°. A nitrogen determination gave:

	Calculated for $C_6H_7NO_2$.	Found.
N	11.2	11.4

This material is, therefore, methylpyromucamide. The corresponding ethylpyromucamide was found by Wallach † to be an oil boiling at 258°.

(2) In another experiment 30 g. of the imido-ester were mixed with 17 g. of methyl iodide and allowed to stand nineteen days. At the end of this time 1 g. of pyromucamide had separated, melting at 140°. The oil filtered from

* Die Imidoäther, p. 50. † Ann. Chem. (Liebig), ccxiv, 229.

this was distilled at 20 mm. pressure. The oil collected below 143° had the odor of the unaltered material, while the remaining portion, between 143° and 148°, solidified and proved to be a mixture of pyromucamide and methylpyromucamide.

The behavior of this ester with methyl iodide is therefore closely similar to that of the preceding.

p-Tolenylimidomethyl Ester. — This ester was prepared from *p*-tolunitril by Pinner's directions. It was obtained as a clear, colorless oil, with an odor entirely different from that of the nitril. It boiled at 105.5° at 10.5 mm. pressure. A nitrogen determination gave:

	Calculated for $C_9H_{11}NO$.	Found.
N	9.39	9.48

p-Tolenylimidomethyl Ester and Methyl Iodide. — 20 g. of the ester were heated to 100° for four hours. A little pressure was found on opening the tube, which was filled with a yellow crystalline mass of material. On crystallizing twice from water (?) this melted from 144° to 145° (the melting-point of *p*-toluic methylamide is given by Gattermann and Schmidt † as 143°). A nitrogen determination gave:

	Calculated for $C_9H_{11}NO$.	Found.
N	9.39	9.36

p-Tolenylimidomethyl Ester and Methyl Alcohol. — 15 g. of the ester were heated with one molecular proportion of methyl alcohol for six hours at from 100° to 110°. As there appeared to be no reaction, the mixture was heated at from 100° to 140° for six hours more, and finally at from 150° to 175° for some time. The material then had the odor of nitril, and it was distilled at 13 mm. pressure, when, after the alcohol escaped, it all boiled from 95° to 97° (the boiling-point of *p*-tolunitril), except a very slight residue. This, crystallized from water, melted at 159°, and was therefore *p*-toluic amide. Under these conditions no rearrangement took place.

* Ann. Chem. (Liebig), ccxliv, 51.

β-Naphthylimidoethyl Ester and Ethyl Iodide. — The ester was prepared from β-naphthonitril, Pinner's directions being followed. It was found that it could be distilled under diminished pressure, but the record of its boiling-point is not at present available to the writer. That it did not suffer decomposition in this treatment is shown by the following nitrogen determination:

	Calculated for $C_{13}H_{13}NO$.	Found.
N	7.0	7.4

The material thus prepared is a clear, colorless oil, and quite stable. 24 g. of this ester were heated with 9.4 g. of ethyl iodide for six hours at 100°. On cooling, the tube was found to contain a solid mass of yellow material. It was treated with alcohol, which left behind a small amount of white crystals which melted above 280°. The soluble part, when crystallized from alcohol, melted constantly at 129°–131°, and is undoubtedly ethyl-β-naphthamide, but a nitrogen determination gave 8.1 per cent of nitrogen. (Calculated for amide 8.2 per cent, for ethyl amide 7.0 per cent.) The lack of sufficient pure material prevented a duplicate analysis.

Experiments with Silver Succinimide and Benzoylbenzimidoethyl Ester.

By Bayard Barnes.

Silver Succinimide and Methyl Iodide. — It was shown by Comstock and Wheeler * that if perfectly dry silver succinimide is treated with alkyl iodides at ordinary temperatures, and especial care is taken to avoid moisture, oxygen esters can be isolated. The formation of a small amount of the nitrogen ester under these conditions was also observed, and it was remarked that "If the nitrogen ether is formed by molecular rearrangement from the oxygen ether, that rearrangement must take place in this case at ordinary temperature." This

* Amer. Chem. Jour., xiii, 519.

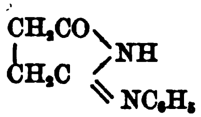
we now know to be the case, since this rearrangement is the chief reaction at high temperatures. For example: 27 g. of the silver salt were heated with 22.8 g. of methyl iodide for six hours at 100°. The material was then extracted with ether and distilled at 20 mm. pressure, when it boiled from 140° to 155°. This readily solidified and, on crystallizing from alcohol, it melted from 68° to 70°. A nitrogen determination gave:

	Calculated for $C_5H_7NO_2$.	Found.
N	12.38	12.45

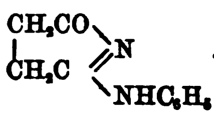
The material is therefore *N*-methylsuccinimide. On extracting the silver residue with alcohol, and crystallizing the extract from benzene, succinimide was obtained.

Silver Succinimide and Ethyl Iodide. — (1) 24 g. of the silver salt and 22.5 g. of ethyl iodide were heated for twelve hours at 100°. As unaltered silver salt still remained, 13.8 g. more iodide were added, and the whole reheated six hours longer. The material was then extracted with benzene and distilled at 20 mm. pressure. The first fraction was collected between 122° and 132°; the second from 132° to 142°; while above 142° the material solidified in the delivery tube.

The first portion was a pale-yellow oil at ordinary temperature, but it solidified on cooling, and, on freezing out of ether, it was obtained in colorless crystals melting at 26° (the melting-point of *N*-ethylsuccinimide). The second fraction was mixed with a little aniline, and the presence of the oxygen ethyl ester established by the formation of crystals, which, after purification by dissolving in hydrochloric acid and precipitating with ammonia, melted at 216°, this substance being the "base" described by Comstock and Wheeler, which perhaps may be called *a*-ketopyrrolidine-*a*-phenylimide or *a*-anilidopyrrolon according to whether it has the structure:



or



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The third fraction or residue was found to consist of succinimide.

(2) In another experiment 30 g. of the silver salt were heated with 45 g. of ethyl iodide for ten hours at from 150° to 155°. The material was then extracted with dry chloroform and the extract distilled at about 20 mm. (?) pressure. The portion boiling below 134° was redistilled at ordinary pressure, when it nearly all came over at 233°–235° (*N*-ethylsuccinimide boils at 234°–235°). A nitrogen determination in this material gave:

	Calculated for $C_6H_9NO_2$.	Found.
N	11.02	10.70

It follows from the above that the oxygen ethers of succinimide undergo rearrangement at high temperatures with methyl and ethyl iodides giving the isomeric nitrogen compounds.

Benzoylbenzimido Ester and Ethyl Iodide. — As an example of the behavior of the acylimido-esters with ethyl iodide, we describe the following experiment. We were unable to discover any evidence of a rearrangement taking place in this case. This is probably due to the negative character of the acyl ester rather than to a stereochemical interference depending on the molecular magnitnde of the =NR grouping. This subject will be investigated later.

Twenty g. of benzoylbenzimidoethyl ester and 6 g. of ethyl iodide were heated for eight hours at from 110° to 120°, when the material was found to be unaltered. It was reheated for seven hours at from 120° to 150° with the same result. Finally, when heated to 200° for six hours, it decomposed. On opening the tube there was considerable pressure and a strong odor of benzonitril. The material was shaken with sodium carbonate and extracted with ether. The solution of sodium carbonate extracted benzoic acid, and the ether took up benzonitril and ethyl benzoate. The amount of benzonitril obtained weighed 5.6 g., while the calculated yield of benzonitril for the following decomposition is 8 g.:

$$C_6H_5C\begin{cases} \!=\!N\,COC_6H_5 \\ -OC_2H_5 \end{cases} = C_6H_5CN + C_6H_5COOC_2H_5.$$

It is our intention to continue the study of these rearrangements in other series.

NEW HAVEN, June 27, 1899.

RESEARCHES ON THE SODIUM SALTS OF THE AMIDES.*

By HENRY L. WHEELER.

THE work described in this paper was undertaken with the object of determining the relative ease with which certain acid amides yield sodium salts, and of determining whether a stereochemical interference is noticeable in this series, by comparing the velocity at which, under given conditions, metameric amides of the form $R{-}NH{-}\underset{\underset{O}{\|}}{C}{-}H$ and $H{-}NH{-}\underset{\underset{O}{\|}}{C}{-}R$ form salts. Such a comparison, taken in connection with a similar examination of the disubstituted formamides,

$$RNHCOR' \quad \text{and} \quad R'NHCOR,$$

in which R = aryl and R′ = alphyl, might be expected to throw new light on the disputed question of the structure of these salts. For example, which one of the above-mentioned isomeric forms is most favorable for the formation of sodium salts, or, in other words, in what position does R have the more retarding effect? And is this effect general for one of these types? If the sodium attaches itself to nitrogen, then R should exert a greater interference when attached to the same atom than when further removed or attached to carbon; for example, formanilide, C_6H_5NHCOH, should then give a salt less easily than benzamide, $HNH{-}COC_6H_5$.

As regards the velocity of formation of the salts, the question of relative acidity or negative character of the molecules arises at once. Do the amides give salts in accordance with the strength of the acids from which they are derived? To what extent does the basic character of the amino group influence

* Amer. Chem. Jour., xxiii, No. 6.

the velocity of formation of the salts?* The latter questions are evidently the first to be decided.

It was necessary at the outset to devise a new method for the preparation of the sodium salts. It was found that sodium amalgam answers the purpose better than metallic sodium; that in boiling benzene the former does not become covered with a coating, as the metal does; and that salts can be prepared by its use which cannot be obtained by any of the previously existing methods.

In order to determine whether acidity is the chief factor in determining the velocity of formation of the sodium salts, the following anilides in molecular proportions, taking 0.5 g. of acetanilide, were dissolved in 100 c.c. of benzene and boiled for one hour with 9 g. of a 4.7 per cent amalgam. The solutions were then filtered as rapidly as possible, and the amount of anilide which had formed sodium salt was determined as described below. The following figures approximately show this amount in percentages, the affinity constants of the respective acids being given for comparison:

	Average of Two Experiments.		K.†
Formanilide, C_6H_5NHCHO,	100	Formic acid,	0.0214
Acetanilide, $C_6H_5NHCOCH_3$,	82	Acetic acid,	0.0018
Oxanilide, $(C_6H_5NHCO-)_2$,	63	Oxanilic acid,	1.21
Benzanilide, $C_6H_5NHCOC_6H_5$,	38	Benzoic acid,	0.006

From this it is evident that the results do not correspond with the strengths of the acids. Thus, oxanilide should give a salt more readily than formanilide and acetanilide, and benzanilide more readily than acetanilide.

That basicity does not exert the most important influence, the acyl radical being the same, is shown by the following results, which were obtained under the same conditions:

* It is well known that the presence of negative groups in the amides favors the formation of salts, dibenzamide, benzoylurethane, etc., are soluble in alkali, while benzamide is insoluble, and again, the acyl cyanamides have stronger acid properties than the acids from which they are derived. Bader, Zeitschr. phys. Chem., vi, 305.

† Ostwald, Ibid., iii, 241.

Benzamide, $H_2NCOC_6H_5$	98
Benzanilide, $C_6H_5HNCOC_6H_5$	38
Benzoylbenzylamine, $C_6H_5CH_2HNCOC_6H_5$	1

	K.*
Ammonia	0.0023
Benzylamine	0.0024

Thus, if the positive character of the molecules determined the velocity of formation of the salts, benzanilide should react more readily than benzamide; and since benzylamine has practically the same basicity as ammonia, the benzoyl compounds should give salts with equal readiness.

It is interesting to note here that Hjelt † found that the rate of saponification of the alkyl malonic esters is not in agreement with the affinity constants of the corresponding acids, but that it agrees, rather, with what would be expected from the theory of stereochemical interference.

In order to determine which one of the two general forms, RNHCOH or HNHCOR, is more favorable for salt formation, the following amides were examined under the same conditions as described above, except that 23 g. of a 0.73 per cent amalgam were used. The figures represent the percentages of amide converted into sodium salt under these conditions:

	Average.
Formanilide, $C_6H_5.NHCO.H$	57
Acetanilide, $C_6H_5.NHCO.CH_3$	8
Propionanilide, $C_6H_5NHCO.C_2H_5$	12
Benzamide, $H.NHCO.C_6H_5$	51
Methylbenzamide, $CH_3.NHCO.C_6H_5$	0
Ethylbenzamide, $C_2H_5.NHCO.C_6H_5$	0

In the following cases the conditions were the same as in the first experiments, using a 4.7 per cent amalgam. In all cases excepting formanilide and benzamide, however, 150 c. c. of benzene were used:

* Bredig, Zeitschr. phys. Chem., xiii, 306.

† Ber. d. chem. Ges., xxix, 1866.

	Average.
Formanilide, C_6H_5NHCOH	100
Orthoformtoluide, $C_6H_4CH_3NHCOH$	96
α-Formnaphthalide, $C_{10}H_7.NHCOH$	99
2,4,6-Trimethylformanilide, $C_6H_2(CH_3)_3NHCOH$	96
Benzamide, $HNHCOC_6H_5$	98
Orthotoluamide, $HNHCOC_6H_4CH_3$	91
α-Naphthamide, $HNHCOC_{10}H_7$	76
2,4,6-Trimethylbenzamide, $HNHCOC_6H_2(CH_3)_3$	88

These results, thus far, show that a disubstituted formamide gives a salt less readily than one that is monosubstituted, which would be expected from the theory of stereochemical interference; and that when the larger or interfering radical is attached to nitrogen it has less effect in retarding the formation of sodium salts than when attached to the keto group. They, therefore, indicate that the sodium is attached to oxygen.* Although it is true that the results all point in this direction, nevertheless the interference which might be expected in certain cases does not exist, while in others an unexpected inertness is shown. An examination of the isomeric cycloamides, oxindol (I) and phthalimidine (II), under the same conditions as in the first experiments, showed that in both cases the amount of amide which had formed salt was practically 100 per cent, while benzoylbenzylamine (III), which has an acyclic structure corresponding to phthalimidine, as already stated, gave practically no salt under these conditions:

$$\overset{\text{I.}}{C_6H_4\left\langle\begin{matrix}NH\\CH_2\end{matrix}\right\rangle CO,}\qquad \overset{\text{II.}}{C_6H_4\left\langle\begin{matrix}CO\\CH_2\end{matrix}\right\rangle NH,}\qquad \overset{\text{III.}}{\left.\begin{matrix}C_6H_5CO\\C_6H_5CH_2\end{matrix}\right\rangle NH.}$$

The interesting results obtained by Remsen and Reid † on the saponification of the substituted benzamides show that substituents in the ortho position "exert a remarkable protective influence on the amide group." The order in which the

* Compare Michael, J. prakt. Chem., lx, 322.
† Amer. Chem. Jour., xxi, 281.

various groups produce a retardation was found to be as follows, in order of decreasing influence: NO_2, —I, $—NH_2$, $—CH_3$, —Cl, —OH, $—O.C_2H_5$, $—O.CH_3$. Unfortunately, for a comparison with the velocity of formation of the corresponding sodium salts, only $—NH_2$, $—CH_3$, and the least interfering groups, $—O.C_2H_5$ and $—O.CH_3$, are probably available for examination by the present method. The results with orthotoluamide indicate, however, that interference also plays a part in the formation of the sodium salt of that compound, although it is not shown in a very decided manner. On the other hand, it is curious that benzoylbenzylamine, and methyl- and ethylbenzamides are so inert, and that they give salts less readily than benzanilide, while the results with trimethylbenzamide are most unexpectedly high.

The derivatives of 2-4-6-trimethylbenzoic acid, like other diorthosubstituted acids, are notably inactive in reactions which are supposed to involve an addition to the keto group.* The acid is not converted into its ester by means of hydrogen chloride and alcohol.† The ester ‡ and amide § are difficult to saponify, while the chloride is remarkably stable towards water and alkalies. Diorthosubstituted acid chlorides in general react readily with ammonia, ‖ however, and the silver salt of trimethylbenzoic acid gives almost a quantitative yield of the ester with methyl iodide.¶ It is assumed that these latter reactions do not involve any addition to the keto group, but take place by direct substitution.** The fact now that 2,4,6-trimethylbenzamide forms a sodium salt practically as readily as orthotoluamide, and that no very decided stereochemical interference is found in this reaction, would suggest that here, also, direct substitution takes place, and that the

* Henry, Ber. d. chem. Ges., x, 2041; Wegscheider, Monatschefte, xvi, 148; Angeli, Ber. d. chem. Ges., xxix, R, 591; Pechmann, Ibid., xxxi, 504.

† V. Meyer, Ibid., xxvii, 510.

‡ Ibid., xxvii, 1263.

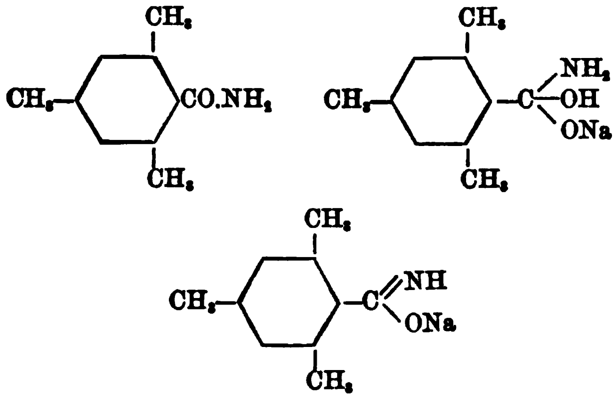
§ Sudborough, J. Chem. Soc. (London), 1897, 229.

‖ Sudborough, Ibid., 1897, 234.

¶ Meyer, Ber. d. chem. Ges., xxvii, 1580.

** Max Scholtz, Der Einfluss d. Raumerfüllung d. Atomgruppen · Sudborough, loc. cit.

sodium is attached to nitrogen. On the other hand, if the sodium is attached to oxygen, the reaction must be an addition of sodium hydrate to the keto group, and then a separation of water, as follows: *



If this is true, it follows that 2,4,6-trimethylbenzamide, out of all harmony with the theory of stereochemical interference, must readily form an addition-product with the alkali. This is precisely what takes place, not only in this case but also with the symmetrical 2,4,6-tribrombenzamide, which Sudborough states exhibits the greatest amount of stereochemical interference, as regards its hydrolysis, of any of the amides examined by him.

The ease with which 2,4,6-trimethylbenzamide forms a sodium salt is therefore in harmony with the theory that the metal in the sodium salts of the amides is attached to oxygen.

I have found that 2,4,6-trimethyl- and tribrombenzamides are readily removed from even their dilute solutions in ether by simply shaking with powdered potassium hydrate, the addition-product being absolutely insoluble in ether. On filtering and treating the residue with water, these compounds undergo dissociation, and the unaltered amides are recovered.

* Naturally a mere trace of moisture would be sufficient, since the water which separates would again react until all the amide is converted by the sodium into salt.

In order to prepare the compound $C_6H_2Br_3CONH_2.NaOH$, it is simply necessary to pour an excess of the amide dissolved in benzene over finely powdered sodium hydrate, whereupon the latter is quantitatively converted into the addition-product.*

This is all the more surprising since Pechmann † found that 2,4,6-trimethylbenzoic ester does not form an addition-product with sodium alcoholate, which is one of the notable properties of ethyl benzoate, and I have found that 2,4,6-tribrombenzoyl chloride and methyl 2,4,6-tribrombenzoate do not give addition-products with potassium hydrate, and also that 2,4,6-tribrom-N-dimethylbenzamide yields no sodium hydrate compound under the same conditions that proved successful with the amide.

The readiness with which the diorthosubstituted amides form addition-products with the alkali, contrasted with their inertness as regards saponification, suggests that the processes involved in the formation of sodium salts and in saponification are not analogous. If we accept the addition theory of saponification, the existence of these alkali addition-products shows that the stereochemical interference in regard to the saponification of these amides, at least with alkali, is not due to a protection from attack, but, for some other specific reason, they give up ammonia with difficulty.

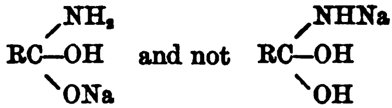
That these alkali addition-products have the elements of the alkali attached to the keto group, and are not merely so-called molecular compounds, is shown by the behavior of the sodium hydrate addition-product of thioacetanilide with benzoyl chloride, which reaction yields acetanilide and thiobenzoic acid, as follows:

$$\begin{array}{lclcc} & \diagup NHC_6H_5 & & \diagup NHC_6H_5 & & CH_3CONHC_6H_5 \\ CH_3C & -OH & \rightarrow CH_3C & -OH & \rightarrow & + \\ & \diagdown SNa & & \diagdown SCOC_6H_5 & & HSCOC_6H_5 \end{array}.$$

*** Interesting also, in this connection, is the fact that Küster and Stallberg (Ann. Chem. (Liebig), cclxxviii, 217) state that 3-nitro-2,4,6-trimethylbenzamide dissolves in aqueous alkali and even in carbonates.**

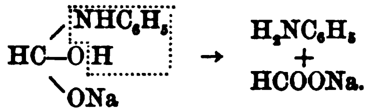
† Loc. cit.

That they have the formula

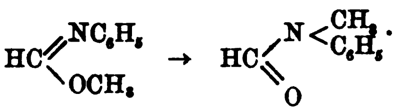


is shown by the behavior* of the addition-products of formanilide, formtoluide, etc.

When heated, or, as found by Tobias,† when simply allowed to stand over sulphuric acid, these compounds decompose as follows:



This formula, as representing the structure of these addition-products is objected to by Cohen and Brittain,‡ since, when heated, the analogous sodium alcoholate addition-products§ lose alcohol and yield sodium acetanilide, ‖ which, with methyl iodide, gives methylacetanilide, methylaniline, etc. Their statement that this formula "would necessitate a molecular change of a very complex character which is scarcely justified by the facts" no longer holds true, since phenylformimidomethyl ester undergoes this rearrangement with methyl iodide, even in the cold, yielding methylacetanilide:



Experimental Part.

Experiments with a 0.73 Per Cent Amalgam.

Formanilide. — The method adopted in general for the determination of the ease with which the amides form salts was

* See also Hantzsch, Ann. Chem. (Liebig), ccxcvi, 91.
† Ber. d. chem. Ges., xv, 2451.
‡ J. Chem. Soc. (London), 1898, clxii.
§ Cohen and Archdeacon, Ibid., lxix, 91.
‖ Seifert, Ber. d. chem. Ges., xviii, 1358.

as follows: 0.4481 g. of formanilide, and the equivalents of the other amides, were dissolved in 100 c. c. of benzene and heated, whereupon 23 g. of a 0.73 per cent amalgam were added. This is somewhat more than twice the calculated quantity of sodium. After boiling one hour, the solution was filtered, and the residue of sodium salt was collected on the filter, while the heavier amalgam was allowed to remain in the flask. The whole was washed with somewhat over 50 c. c. of warm benzene by means of a wash-bottle and the filtrate evaporated in a weighed flask, the residue being dried in a stream of air at ordinary temperature. In most cases the residue consisted of unaltered amide, which gave directly the weight of material not forming sodium salt. In all cases this residue, after weighing, was treated with water and titrated with a standard hydrochloric acid solution, using an aqueous solution of the sodium salt of orthonitrophenol as indicator, which recommended itself, since it gives a very sharp end-reaction by gaslight and carbonic acid does not interfere except in the cold.

In this manner the amount of sodium salt dissolved by the benzene was determined and the correction made. The amount of amide forming sodium salt was then determined by difference. In some of the experiments the amount of anilide recovered, after boiling with amalgam, was determined by saponifying the anilide with strong hydrochloric acid, and then determining the amount of aniline volumetrically by means of a standardized solution of potassium bromate and bromide.*

Two experiments with formanilide, performed as above, gave 0.1963 and 0.1859 g. anilide not attacked, corresponding to 56 and 58 per cent as sodium salt. This sodium salt is insoluble in benzene.

It must be understood that the quantitative results given in this paper are merely approximate, and in certain cases it is difficult to get closely agreeing results. The first difficulty encountered is the fact that with the solid amalgam it is diffi-

* Reinhardt, Zeitschr. anal. Chem., xxxiii, 90; compare François and Denigès, J. Soc. Chem. Ind., xviii, 866.

cult to get the same state of division each time, although in each case the amalgam was freshly powdered and passed through a moderately fine sieve before it was used. A curious result was observed when two different preparations of a semi-solid amalgam was used, both containing the same percentage of sodium as far as could be determined; *i. e.*, 0.72 and 0.73 per cent. By means of the latter, when acetanilide was boiled for one hour, 8.7 and 8.0 per cent were found to have been converted into sodium salt; with the former preparation, however, on boiling for two hours three experiments each gave 3.9 per cent as the amount of anilide that had been attacked.

It has previously been observed that certain preparations of sodium amalgam have given widely different results in reduction experiments,* and Aschan † explains this by the assumption that impurities cause the evolution of hydrogen in the molecular form and not in an active state. This explanation fails in the above case. With these results, which fortunately occurred at the beginning of the work, all the comparisons were afterward made with portions of the same preparations.

Other sources of error are as follows: The sodium salts are bulky, gelatinous, and difficult to wash when prepared in this way; therefore the small quantities of amides used in the experiments, and, in some cases, the residues left on evaporating the benzene, are difficult to dry. In no case was any reduction of the amide observed, as in the case when the amides are acted on with amalgam in acid ‡ or alkaline § solutions.

Acetanilide. — When two experiments with 0.5 g. of this anilide were performed as described above, 8.7 and 7.9 per cent of the anilide were found to have been converted into sodium salt. This quantity was all dissolved in the benzene solution. Experiments at 20°, the other conditions being exactly the same, gave peculiar results. It was found that 17.8

* Lassar-Cohn, Lab. Manual Org. Chem., p. 308.

† Ber. d. chem. Ges., xxiv, 1866.

‡ Guareschi, Ibid., vii, 1462.

§ Hutchinson, Ibid., xxiv, 173.

and 20.8 per cent of the acetanilide had been converted into sodium compound, or about two and one-half times as much as at the temperature of boiling benzene. The explanation of this was found on filtering the benzene solution, when before the washing was complete the sodium hydrate addition-product mentioned by Cohen and Brittain ‖ began to separate. This owed its formation to the unavoidable presence of moisture absorbed by the amalgam and benzene during the manipulation. These authors state that the alkali addition-products are readily dissociated at the temperature of boiling ether; therefore, all other experiments described here were performed at the temperature of boiling benzene.

The sodium hydrate addition-product of acetanilide is soluble in benzene, while that of formanilide is insoluble; therefore, at temperatures at which the intermediate addition-products are stable, more sodium compound should be formed in the case of acetanilide than with formanilide, when treated with metallic sodium covered with a layer of sodium hydrate. The results of the following experiments proved this to be true. The anilides were dissolved in 100 c.c. of benzene (0.4481 g. formanilide and 0.5 g. acetanilide) and shaken in a machine for one hour, with 0.5 g. of sodium weighed in the air, whereupon formanilide gave 5.3 and 5.9 per cent, and acetanilide 20.5 and 26.3 per cent anilide as sodium compound.

Propionanilide. — One experiment with 0.5518 g. of this anilide, which was performed in boiling benzene, gave no turbidity or separation of salt from the benzene solution, but on filtering and evaporating, 12.2 per cent was found to have been converted into salt.

Benzamide. — In this case two experiments with 0.4481 g. of material gave 1.4 per cent of amide as sodium compound dissolved in benzene and 49.1 and 50.2 undissolved; total, 50.5 and 51.6.

Methyl- and Ethylbenzamides gave no evidence of any salt formation under the above conditions. The benzene solution was found to be free from alkali, and, on evaporating off the

‖ Loc. cit.

benzene, the weights of the residues came from 2 to 5 per cent too high, it being difficult to dry the material without loss.

Experiments with a 4.7 Per Cent Amalgam.

Formanilide. — In each of the following experiments 9 g., or five times the calculated quantity of amalgam, were used. 0.4481 g. of this anilide, when treated as above, gave no residue on evaporating the benzene; hence the amount of salt formed was 100 per cent.

Acetanilide. — One-half g. gave, in two experiments, 29.6 per cent as salt dissolved in the benzene, and 48.1 per cent undissolved in one; and 29.6 and 56.8 per cent in another; total, 77.7 and 86.4; average, 82. Lack of better agreement is due to the difficulty of drying, owing to the amount of salt dissolved by the benzene.

Oxanilide.— In two experiments 0.4444 g. gave 65.4 and 60.0 as monosodium salt. This salt is insoluble in benzene; it was separated from all but traces of the amalgam by decantation, and a sodium determination gave:

	Calculated for $C_6H_5NHCOCONaNC_6H_5$.	Found.
Na	8.8	9.1

Water decomposes the salt,* liberating anilide.

Benzanilide. — Attempts to prepare a sodium salt for synthetical purposes by boiling this anilide in benzene with sodium were unsuccessful. Quantitative experiments indicated that over 95 per cent of the anilide was unaltered. The use of xylene, as recommended by Hepp,† gave no better result. The method of Seifert ‡ and Blacher § for the preparation of sodium salts also failed in this case. It was prepared, however, by boiling the concentrated benzene solution with an 8 per cent amalgam. 10 g. anilide gave about 7 g. of

* In determining the amount of sodium in the following new salts, which was done volumetrically, a determination of the amount of mercury was also necessary in some cases; in others this was very small and was disregarded. The decanted precipitates always contain more or less mercury.

† Ber. d. chem. Ges., x, 328.

‡ Ibid., xviii, 1357.

§ Ibid., xxviii, 435.

salt after boiling several hours. It was separated from the excess of amalgam by decantation. As the amalgam used was not freshly prepared and contained some sodium hydrate, the results on analysis came high. The percentage of sodium calculated is 10.5; found, 11.7. In the experiments of Paal and Otten * on the action of acyl chlorides on the sodium salts of the anilides, they invariably treated the salt of a lower anilide with a chloride of higher acid, benzoyl chloride with sodium acetanilide, sodium formanilide, etc., and obtained nothing but the anilide of the higher acid. The action proved to be abnormal, as diacyl anilides were not obtained. It seemed of interest, therefore, to try the action of acetyl chloride on sodium benzanilide under the same conditions as described by the above authors, and it was found that the action was also abnormal in this case, and that nothing but benzanilide was obtained.

Quantitative experiments with 0.7296 g. anilide, on the formation of sodium benzanilide, gave 35.3 as the amount of amide which had formed salt, in one, and 40.5 per cent in another; average, 37.9. The salt is insoluble in benzene; it is bulky and gelatinous, but when dried forms a white, amorphous powder.

Benzamide. — The amide (0.4481 g.) gave 98 per cent as the amount that had formed salt, while 1.4 per cent of the amide was in solution as sodium salt. After decanting the bulky, gelatinous salt and rapidly drying in a steam oven, a sodium determination gave:

	Calculated for C_7H_6NONa.	Found.
Na	16.0	16.2

Ethylbenzamide. — Two experiments with 0.5518 g. each of this amide, again with the stronger amalgam, gave no evidence of any salt formation. On boiling the benzene solution it remained perfectly clear, and on examining the residue left on evaporating the benzene it was found that less than 0.7 per cent of the amide had formed salt.

* Ber. d. chem. Ges., xxiii, 2587.

Benzoylbenzylamine. — This was prepared by the Baumann-Schotten reaction. Two experiments with 0.7815 g. of material gave perfectly clear solutions on boiling with the amalgam, and an examination of the residue, on evaporating the benzene solution, indicated that in both cases 1.0 per cent of the amide had been converted into sodium salt. The recovered material melted sharply from 106° to 107°.

Oxindol. — This cycloamide (0.4926 g.) gave a bulky, gelatinous separation of salt immediately on warming and, on evaporating the filtered solution, the residue weighed 0.0050 g. It was found to be free from alkali, and, therefore, 99 per cent of the amide was converted into salt. A sodium determination gave:

	Calculated for C_8H_6NONa.	Found.
Na	14.8	15.3

Phthalimidine. — This amide (0.4926 g.) gave a bulky, gelatinous salt, like the above, and the recovered residue of unaltered material weighed 0.0066 g.; hence 98.7 per cent of the amide formed salt. A sodium determination gave:

	Calculated for C_8H_6NONa.	Found.
Na	14.8	14.8

Phenyloxamide. — This amide (0.3037 g.) refused to dissolve completely in 100 c. c. of benzene before adding the amalgam, so that the results are not directly comparable with the above. The amount of amide converted into salt was found to be 57.3 per cent.

Oxamide and *phthalamide* are insoluble in benzene. *Formamide* * immediately liberates ammonia, while *acetamide* appears to be less readily decomposed by the above treatment.

The following experiments required the use of 150 c. c. of benzene, owing to the difficulty with which *a*-naphthamide dissolves in this solvent.

* That this amide gives a sodium salt with great ease, by a less energetic reaction, is shown by the method used by Freer and Sherman (Amer. Chem. Jour., xviii, 580).

Orthoformtoluide. — This was one of the few cases in which the amalgam showed any tendency to "cake," or the salt to attach itself to the amalgam; nevertheless, 0.5 g. gave 95.7 per cent as the quantity of toluide forming sodium salt; 3 per cent of this was dissolved by the benzene. The salt separated by decantation gave:

	Calculated for C_8H_8NONa.	Found.
Na	14.6	14.2

Orthotoluamide. — This was prepared by the method suggested by Remsen and Reid. The amount used was 0.5 g., and 90.6 per cent of this was found to have formed sodium salt. No salt was found in the benzene solution. A sodium determination gave:

	Calculated for C_8H_8NONa.	Found.
Na	14.6	15.1

a-Formnaphthalide. — Of this, 0.6333 g. gave 98.9 per cent as sodium salt. It is bulky and gelatinous, and therefore filters slowly. Less than 1 per cent of salt was found in the benzene. A sodium determination gave:

	Calculated for $C_{11}H_8NONa$.	Found.
Na	11.8	12.2

a-Naphthamide. — The nitrile was prepared from *a*-naphthylamine by the Sandmeyer reaction. Of the amine 85.8 g. gave 13 g. of nitrile boiling at about 300°. When this was dissolved in an excess of alcoholic sodium hydrate and warmed for a few minutes, the first separation of crystals weighed 5 g. and were practically pure amide, melting at 202°.

The amide (0.6333 g.) gave 23.6 per cent unaltered material. After being heated as above, this melted sharply at 202°. The amount of amide as sodium salt was therefore 76.4 per cent. A sodium determination gave:

	Calculated for $C_{11}H_8NONa$.	Found.
Na	11.8	12.4

2,4,6-Trimethylformanilide. — The mesidine was prepared by heating trimethylphenylammonium iodide at 210° with a few drops of methyl alcohol. It is more readily obtained from mesitylene by nitration and reduction. The formyl compound melted at 177°. Of this, 0.6037 g. gave 95.9 per cent as sodium salt, which separated as a bulky, gelatinous mass. Less than 1 per cent of this was dissolved by the benzene. A sodium determination gave:

	Calculated for $C_{10}H_{12}NONa$.	Found.
Na	12.4	12.3

2,4,6-Trimethylbenzamide. — For the preparation of this amide mesitylene was nitrated according to the method of Schulz.* After distilling in steam, the oil obtained was distilled at 15–20 mm. pressure, when the fraction, 120°–130°, was collected. It boils for the most part at 150°–154° at about 50 mm. pressure. 131 g. of mesitylene gave 61 g. of crude nitro-compound. This, on reduction, gave 25.3 g. of mesidine boiling from 224° to 226° (uncorr.). From this the nitrile was prepared according to Sandmeyer's reaction, using the conditions of Liebermann and Birukoff † for the preparation of the corresponding 2,4-xylylic nitrile. They obtained a yield of 50–60 per cent. In the present case the yield was far below this, about 8 g. of crude nitrile being obtained. On boiling this for seventy-two hours with alcoholic potash, the first separation of crystals, on cooling and crystallizing the product from benzene, weighed 2 g. and melted sharply from 187° to 188°.

When 0.6037 g. of this amide was treated with the amalgam, an immediate turbidity of the benzene solution resulted, and an extremely gelatinous precipitate separated which was difficult to wash. The salt is absolutely insoluble in benzene, and 87.8 per cent of the amide was converted into salt. A sodium determination gave:

	Calculated for $C_{10}H_{12}NONa$.	Found.
Na	12.4	12.8

* Ber. d. chem. Ges., xvii, 477. † Ann. Chem. (Liebig), ccxl, 286.

2,4,6-Trimethylbenzamide and Potassium Hydrate. — It was found that this amide readily unites with alkali in the following way: Potassium hydrate was used, as Cohen states that these addition-products, in the case of the substituted acetanilides, are more soluble than the sodium hydrate compounds. Of this amide 0.3003 g. was dissolved in 100 c. c. of ether, in which it is readily soluble, and 2 g. of potassium hydrate were powdered under 40 c. c. of ether and then the whole mixed together. The mixture was shaken for half an hour and then filtered into a weighed flask. It was washed with 100 c. c. of ether and, on evaporating the ether and drying the residue in a stream of air for a few minutes, 0.0115 g. of unaltered amide was recovered; 96.2 per cent had, therefore, combined with the alkali. On treating the alkali with water the amide was recovered.

2,4,6-Tribrombenzamide. — This was prepared from metaminobenzoic acid. Tribrombenzoic acid was prepared by eliminating the amino group from this after brominating.* 20 g. of aminobenzoic acid gave 52 g. of the tribromamino acid melting at 170°–172°, and this gave 48 g. of crude tribrombenzoic acid. This was converted into the chloride in the usual way, and, instead of attempting to purify this by crystallizing from petroleum ether, in which the compound is readily soluble, it was distilled † under a pressure of 35–40 mm., when the chloride boiled from 200° to 210°. On cooling the distillate, beautiful, four-sided tables separated, melting at about 47°. These were crystallized from petroleum ether. The yield was 25 g. The amide separated immediately when this material was dissolved in alcoholic ammonia, and it melted sharply from 191° to 192°.

This amide is the most difficult to saponify of any yet examined; nevertheless it unites with alkali to form addition-products with the greatest ease.

2,4,6-Tribrombenzamide and Potassium Hydrate. — 1.0040 g. of the amide were dissolved in 100 c. c. ether, and 2 g. of potas-

* Volbrecht, Ber. d. chem. Ges., x, 1708.
† Sudborough, loc. cit.

sium hydrate, powdered under 40 c. c. of ether, were added. After shaking for half an hour the material was filtered and washed with 100 c. c. of ether. On evaporating the filtrate only 0.0145 g. of residue was obtained. Therefore, 98.7 per cent of the amide had formed an addition-product with the alkali, and was filtered off.

2,4,6-Tribrombenzamide Sodium Hydrate, $C_6H_2Br_3CONH_2.NaOH$. — These addition-products can be isolated in a state of purity, as follows: 4 g. of the amide are dissolved in 150 c. c. of benzene, and the solution poured on 0.3 g. of pure sodium hydrate in a mortar (calculated quantity, 0.4 g.). The alkali is thoroughly powdered, and then the mass is filtered and washed with benzene, in which the addition-product is insoluble. On drying rapidly in a steam-bath, a sample thus prepared gave the following result on determining sodium hydrate:

	Calculated for $C_6H_2Br_3CONH_2.NaOH$.	Found.
NaOH	10.0	10.3

Under the microscope the material appeared minutely crystalline, but no definite form could be observed. It was absolutely free from the characteristic needles of the free amide. Water immediately decomposes the compound.

2,4,6-Tribrom-N-dimethylbenzamide, $C_6H_2Br_3CO.N(CH_3)_2$. — This was prepared by treating the acid chloride with an excess of an aqueous 33 per cent solution of dimethylamine mixed with methyl alcohol. The product thus obtained was purified by crystallizing from a mixture of benzene and petroleum ether, whereupon well-developed, colorless prisms separated melting from 85° to 86°. A nitrogen determination gave:

	Calculated for $C_9H_8Br_3NO$.	Found.
N	3.61	3.57

When 2 g. of this amide were dissolved in 30 c. c. of benzene and treated with 1.5 g. powdered sodium hydrate, no addition took place. The alkali was free from amide on

filtering and washing, and the benzene solution contained no alkali.

2,4,6-Tribrombenzoyl Chloride and Potassium Hydrate.—1.1020 g. of the chloride were dissolved in 50 c. c. of ether, and 2 g. of potassium hydrate, powdered under 40 c. c. of ether, were added. After twenty minutes the mixture was filtered, washed with 100 c. c. of ether, and the ether evaporated, when the residue weighed 1.0620 g. No alkali was found in this residue; hence 96.3 per cent of the chloride remained unaffected in this treatment.

2,4,6-Methyltribrombenzoate and Potassium Hydrate.—1.0055 g. of the ester were treated with 2 g. of powdered potassium hydrate, as above described, when 0.9841 g. of unaltered material was recovered, or 97.8 per cent.

Thioacetanilide Sodium Hydrate, $CH_3CS—NHC_6H_5.NaOH$.—1.2 g. of sodium hydrate (calculated 1.7) were powdered under a solution of 6.6 g. of thioacetanilide in 30 c. c. of benzene. A finely divided precipitate formed at once, which was very slow in filtering. It was washed with a little ether and dried at about 55°, whereupon a sodium determination gave:

	Calculated for $C_8H_9NS.NaOH$.	Found.
Na	12.0	11.8

Thioacetanilide Sodium Hydrate and Benzoyl Chloride.—5.2 g. of the above were mixed with 3.5 g. of benzoyl chloride in 30 c. c of ether, whereupon reaction immediately set in with evolution of heat. On filtering and evaporating the ether a yellow oil was obtained, which, on standing over night, deposited a mass of needles or prisms. When these were washed with ether and crystallized from water, broad, colorless plates of acetanilide were obtained melting at 114°. The yellow oil was easily recognized as thiobenzoic acid by its peculiar, disagreeable odor. It could not be distilled even under diminished pressure. When it was mixed with aniline in the cold, it gave benzanilide.

The above sodium-hydrate addition-product appears to be

formed when sodium alcoholate and thioacetanilide in alcohol are precipitated with moist ether. A portion prepared in this manner by Dr. P. T. Walden and treated with benzoyl chloride gave the same result as above. A determination of nitrogen in the crystals obtained proved that the material was acetanilide.

NEW HAVEN, February 28, 1900.

ON THE MOLECULAR REARRANGEMENT OF THE THIONCARBAMIC, THIONCARBANILIC, AND THIONCARBAZINIC ESTERS: β-ALKYL-α-μ-DIKETOTETRAHYDROTHIAZOLES.*

By HENRY L. WHEELER AND BAYARD BARNES.

In a recent paper we showed that the thioncarbamic esters, $H_2NCS.OR$, undergo a molecular rearrangement in the presence of alkyl halides, with great ease, giving the isomeric thiol compounds, $H_2NCO.SR$. In this paper we describe the results of an examination of certain monosubstituted xanthogenamides, XNHCS.OR, under similar conditions, and of the preparation of some homologues of "mustard-oil acetic acid" or α-μ-diketotetrahydrothiazole.

We find, when X in the above formula is C_6H_5—, that these compounds, the thioncarbanilic esters, react less readily than the non-substituted thioncarbamic esters. With methyl and ethyl iodides they require more or less protracted heating, while with isobutyl iodide no rearrangement was observed. In order to extend our knowledge of the thion esters, we examined also the phenylthioncarbazinic esters, C_6H_5NH—NHCS.OR, in which X is the positive grouping C_6H_5NH.

Of the three possible types of phenylthiocarbazinic esters certain dithio† and thiol ‡ compounds have been described, but methods were lacking for the preparation of the thion derivatives. It seemed probable that these compounds would result by the action of phenylhydrazine on the dithiocarbonic esters, although the reaction, if taking place between equal molecules and if confined to the β-amino group, and excluding tautomeric forms, might still proceed in four different ways,

* Amer. Chem. Jour., xxiv, No. 1.

† Busch, Ber. d. chem. Ges., xxviii, 2635.

‡ Busch and Stern, J. prakt. Chem., lx, 242.

the dithio ester and the phenylhydrazine first combining to form an addition-product, then decomposing as follows: *i. e.* with the evolution of mercaptan (I or II), or alcohol (III), or hydrogen sulphide (IV):

$$
C_6H_5NH{-}NH{-}C\begin{cases} SC_2H_5 \\ SH \\ OC_2H_5 \end{cases}
\begin{array}{l}
\nearrow\ C_6H_5NH{-}NHCS.OC_2H_5,\ \text{I.} \\
\nearrow\ C_6H_5NH{-}NHCO.SC_2H_5,\ \text{II.} \\
\searrow\ C_6H_5NH{-}NHCS.SC_2H_5,\ \text{III.} \\
\searrow\ C_6H_5NH{-}N{=}C{<}{\substack{SC_2H_5 \\ OC_2H_5}},\ \text{IV.}
\end{array}
$$

In fact, it was found that this reaction proceeds chiefly in the sense of the first and last representations, a solid and an oil being obtained. The solid material is the phenylthioncarbazinic ester (I). This reacts readily with methyl iodide, ethyl iodide, benzyl chloride, etc., giving the phenylthiolcarbazinic esters just described by Busch and Stern: *

$$C_6H_5NH{-}NHCS.OC_2H_5 + IR = C_6H_5NH{-}NHCO.SR + C_2H_5I.$$

This molecular rearrangement takes place at ordinary temperatures, and, therefore, more readily than in the case of the thioncarbanilic esters, a basic character of the molecules being more favorable for rearrangement than a negative one.

Phenylthioncarbazinicethyl ester (I), reacts with phosgene in toluene, giving ethoxyphenylthiobiazolone (V), a representative of a new type of alkyloxythiobiazolones, the other theoretically possible types having been described by Busch. The carbazinic ester reacts with benzoyl chloride, evolving ethyl chloride, but the evolution of this gas is due to a secondary reaction, the chief product obtained being a benzoyl derivative (VI). The same benzoyl derivative is formed from the sodium salt of the carbazinic ester and benzoyl chloride:

V.

$$
\begin{array}{l}
C_6H_5N{-\!-\!-}N \\
\quad | \qquad\ \ \| \\
\ OC{-}S{-}C{-}OC_2H_5
\end{array}
$$

VI.

$$
\begin{array}{l}
C_6H_5{-}N{-}NHCS.OC_2H_5 \\
\qquad\ \ | \\
C_6H_5{-}CO
\end{array}
$$

* Loc. cit.

The formula VI is assigned to the benzoyl compound because it is soluble in alkali and can be precipitated unaltered by acids. That the benzoyl group is not attached to sulphur is shown by the fact that the compound can be boiled with alkali or acids without decomposition.

The action of acyl chlorides is tautomeric when compared with the behavior of the alkali salts of the carbazinic ester with alkyl iodides, for, if phenylthioncarbazinicethyl ester is treated with ethyl iodide in the presence of alcoholic potash, the following represents the course of the reaction:

$$C_6H_5NH-N=C\begin{matrix}\diagup SK \\ \diagdown OC_2H_5\end{matrix} \rightarrow C_6H_5NH-N=C\begin{matrix}\diagup SC_2H_5 \\ \diagdown OC_2H_5\end{matrix}.$$

The oil thus obtained is identical in every respect with the hydrazone (IV), obtained by the direct action of phenylhydrazine on diethyl dithiocarbonate. This behavior is, therefore, similar to that of the thioncarbanilic * and the dithiocarbazinic esters,† but it differs from that of the oxygen analogues,‡ inasmuch as the latter give nitrogen alkyl derivatives.

When the above hydrazone is treated with thiobenzoic acid, a peculiar reaction takes place and phenylthiolcarbazinicethyl ester (II), and ethylthiol benzoate are almost quantitatively obtained. The hydrazone and the thio acid combine at the double bond, then separate as follows:

$$C_6H_5NH-NH-C\begin{matrix}\diagup SC_2H_5 \\ -SCOC_6H_5 \\ \diagdown OC_2H_5\end{matrix} \rightarrow \begin{matrix}C_6H_5CO.SC_2H_5 \\ + \\ C_6H_5NH-NHCO.SC_2H_5\end{matrix}.$$

A similar reaction takes place with thioacetic acid. In addition to the above reaction a small amount of hydrogen

* Liebermann, Ann. Chem. (Liebig), ccvii, 148; Fromm and Block, Ber. d. chem. Ges., xxxii, 2212.

† Busch and Lingenbrink, Ber. d. chem. Ges., xxxii, 2620.

‡ Hantsch and Mai, Ibid., xxviii, 977.

sulphide is evolved, but no acetyl- or benzoylhydrazone was isolated.

The hydrazone can be changed back to the thioncarbazinic ester by passing hydrogen sulphide into the material heated to 125°, or it can be converted into the thiol ester by treating it with hydrogen chloride in benzene solution. These reactions involve the formation of the following addition-products, which decompose in the two opposite ways, as follows:

$$\begin{array}{c}\text{VII.}\\ \begin{array}{l} C_2H_5S\diagdown \\ \quad H\,S{-}C{-}HN{-}NHC_6H_5 \\ C_2H_5O\diagup \end{array}\end{array} \qquad \begin{array}{c}\text{VIII.}\\ \begin{array}{l} C_2H_5S\diagdown \\ \quad Cl\ \ {-}C{-}HN{-}NHC_6H_5. \\ C_2H_5O\diagup \end{array}\end{array}$$

In the case of the action with hydrogen chloride the addition-product (VIII) was isolated; and in the absence of moisture this is stable at temperatures below 57°.

The hydrazone reacts energetically with acetyl and benzoyl chlorides and in the same manner as in the case of the substituted imido-esters, inasmuch as ethyl chloride is evolved and a N-acyl derivative is formed. That the ethyl group attached to oxygen is the one evolved as ethyl chloride in this reaction, and not the group attached to sulphur, is shown by the fact that on boiling the benzoyl derivative with hydrochloric acid phenylthiolcarbazinicethyl ester (II) is obtained. The benzoyl compound, therefore, has one of the following thiol structures:

$$\begin{array}{c}\text{IX.}\\ C_2H_5S.CO{-}NH{-}N\begin{array}{l}\diagup C_6H_5\\ \diagdown COC_6H_5\end{array}\end{array} \quad \text{or} \quad \begin{array}{c}\text{X.}\\ \begin{array}{r}C_2H_5S.CO\diagdown\\ C_6H_5CO\diagup\end{array}N{-}NHC_6H_5.\end{array}$$

This is confirmed by the fact that the thiol compound,

$$C_6H_5NH{-}NHCO.SC_2H_5,$$

reacts smoothly with benzoyl chloride, hydrogen chloride being evolved, and the above benzoyl derivative is formed. That the structure represented by formula IX is probably the correct one, or, in other words, that the acyl groups are

in the α-β-positions in respect to each other, is shown by the acid properties of the compound; it dissolves in alkalies and can be precipitated, even after boiling, unaltered by acids, although a diacyl derivative corresponding to the formula X would be expected to be formed here from analogy with the imido-esters. This, however, would probably be insoluble in alkali.

The following, therefore, represents the action of the hydrazone with benzoyl chloride, the addition taking place with the formation of a pentavalent nitrogen product (XI), and not at the double union as represented in the case of the isoanilides;* this product then rearranges with loss of ethyl chloride, as shown in formula XII:

$$\overset{\text{XI.}}{\begin{matrix}C_2H_5S \\ C_2H_5O\end{matrix}\!>C{=}N{-}\underset{Cl\;\;COC_6H_5}{\overset{}{NHC_6H_5}}} \rightarrow \overset{\text{XII.}}{\begin{matrix}C_2H_5S\diagdown \\ Cl{-}C{-}NH{-}N\!<\!\begin{matrix}C_6H_5\\COC_6H_5\end{matrix}. \\ C_2H_5O\diagup\end{matrix}}$$

The thiocarbazinic esters and the hydrazone are very reactive with compounds of a negative character, but, on the other hand, with bases they show little tendency to react.

Libermann and Voltzkow,† who investigated the action of chloracetic acid on "phenylsulfurethan," and Langlet,‡ who examined the behavior of xanthogenamide with bromacetic acid and β-iodpropionic acid, represented the amides as acting in the pseudoform, and hydrogen chloride as separating in the first stage of the action. It was suggested, however, by P. Meyer § that this reaction probably takes place first with the separation of alkyl halide, and this we find to be the case. For example, chloracetic acid reacts with xanthogenamide at 100° in the same manner as with alkyl halides, and there is no reason for assuming, from this reaction, that the thioncarbamic esters have the pseudoform, the reaction taking place as follows:

* Wheeler and Walden, Amer. Chem. Jour., xix, 130.

† Ann. Chem. (Liebig), ccvii, 137. ‡ Ber. d. chem. Ges., xxiv, 3849.

§ Ibid., xiv, 1663.

XIII.

$$H_2NCS.OC_2H_5 \rightarrow \begin{array}{l} \qquad\qquad\quad \diagup CH_2COOH \\ H_2NC{-}S{-}\boxed{\begin{array}{l}Cl\\ C_2H_5\end{array}} \\ \qquad\quad \diagdown O \end{array} \rightarrow H_2NCO.SCH_2COOH.$$

The carbaminthiolglycollic acid (XIII), thus formed, which was isolated, loses water, giving the ring-formed compound, *α-μ*-diketotetrahydrothiazole (Senfölessigsäure).*

$$\begin{array}{c} \text{XIV.} \\ \begin{array}{l} S\text{———}CONH \\ | \\ CH_2CO{-}\boxed{\begin{array}{l}H\\ OH\end{array}} \end{array} \end{array} \rightarrow \begin{array}{c} \text{XV.} \\ \begin{array}{l} S{-}CO \diagdown \\ | \qquad\qquad NH. \\ CH_2CO \diagup \end{array} \end{array}$$

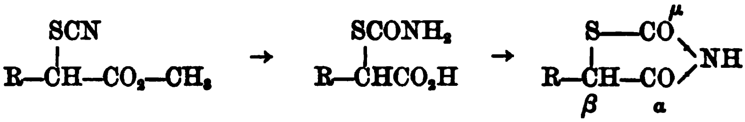
Since the acids XCH_2COOH and XCH_2CH_2COOH react readily with xanthogenamide and phenylxanthogenamide, it seemed of interest to determine whether the homologues of the above ring or the *β*-alkyl derivatives would result in the same manner by employing the halogen acids RCHXCOOH and their esters. It is our experience, however, that these latter compounds react by no means as smoothly as the former; at any rate, a large part of the xanthogenamide undergoes a rearrangement into the corresponding thiol ester and decomposition occurs, giving cyanuric acid, thiol acid, and other products.

We find, however, that the *α*-sulphocyan derivatives of the fatty acid esters, at least the lower members of the series, are capable of the same transformation under the influence of hydrochloric acid as that observed by Heintz † and Claesson ‡ in the case of sulphocyanethyl acetate, and that by this means the homologues in question can be prepared. The methyl and ethyl esters give the best yields of the *β*-alkyl-*α*-*μ*-diketotetrahydrothiazoles, the hydrolysis probably taking place as follows:

* Compare Hantsch and Aripides, Ann. Chem. (Liebig), ccxlix, 8.

† Ann. Chem. (Liebig), cxxxvi, 232.

‡ Ber. d. chem. Ges., x, 1352.



Experimental Part.

Phenylthioncarbazinicethyl Ester, $C_6H_5NH{-}NHCS.OC_2H_5$. —115 g. of xanthogenic ester, $C_2H_5SCS.OC_2H_5$, and 80 g. of phenylhydrazine were warmed for twelve hours on the steam-bath, when hydrogen sulphide and ethyl mercaptan were evolved, and, on cooling, 77 g. of the carbazinic ester separated. This was filtered on the pump and separated from the hydrazone, which latter, after washing with alkali, was dried at 100° in a vacuum, when the oil thus obtained weighed 37 g.

The carbazinic ester was purified by crystallizing from ligroïn or alcohol, from which solvents it separates in the form of needles melting at 72° to 74°. A nitrogen determination then gave:

	Calculated for $C_9H_{12}N_2OS$.	Found.
N	14.2	14.1

This compound dissolves in alkali and is precipitated unaltered by acids.

Phenylthiolcarbazinicmethyl Ester, $C_6H_5NH{-}NHCO.SCH_3$. —This compound was obtained when 2 g. of the above ethyl ester were dissolved in 5 g. of methyl iodide. On standing for several hours and then evaporating the methyl iodide, colorless needles melting at 152° were obtained. In spite of the fact that a nitrogen determination came low (analysis A) this material is identical with that prepared from potassium thiolcarbazinate, $C_6H_5NH{-}NHCO.SK$, and methyl iodide (analysis B) which was first obtained in the latter way by Busch and Stern.*

	Calculated for $C_8H_{10}N_2OS$.	Found. A.	Found. B.
N	15.3	14.7	15.5

* Loc. cit.

Phenylthiolcarbazinicethyl Ester, $C_6H_5NH-NHCO.SC_2H_5$, when prepared by treating the thioncarbazinic ester or the salt, $C_6H_5NH-NHCOSK$, with ethyl iodide, was obtained in needles melting at 112°. Busch and Stern give 113°. A nitrogen determination gave:

	Calculated for $C_9H_{12}N_2OS$.	Found.
N	14.2	14.0

This compound is insoluble in alkali. When this and the preceding compound were heated with molecular proportions of aniline, on the steam-bath, carbanilide was obtained.

Phenylthiolcarbazinicbenzyl Ester, $C_6H_5NH-NHCO.SCH_2C_6H_5$.—When 3 g. of the thion ester were heated with 1.9 g. of benzyl chloride on the steam-bath, ethyl chloride was evolved and the mixture soon solidified. On crystallizing then from alcohol, clusters of spears or needles were obtained melting at 170°, as stated by Busch and Stern. A nitrogen determination gave:

	Calculated for $C_{14}H_{14}N_2.OS$.	Found.
N	10.8	10.0

Ethoxyphenylthiobiazolone, $\begin{array}{l} \quad C_6H_5N-N \\ \quad / \qquad \| \\ OC-S-C-OC_2H_5 \end{array}$.—5 g. of the thioncarbazinic ester and 13 g. of a 20 per cent solution of phosgene in toluene were heated on the steam-bath for half an hour. On evaporating the solvent in a vacuum, an oil was obtained which finally solidified. The material then crystallized from alcohol in colorless prisms which melted constantly at 38°, and a nitrogen determination gave the following result:

	Calculated for $C_{10}H_{10}N_2O_2S$.	Found.
N	12.6	12.3

Phenylthioncarbazinicmethyl Ester, $C_6H_5NH-NHCS.OCH_3$.—When methylethyl dithiocarbonate, $CH_3OCS.SC_2H_5$, was warmed with phenylhydrazine and then cooled, nothing but an oil was obtained. However, on treating this with ether

and alkali, a solid separated which was identical with the above described thiolcarbazinicmethyl ester melting at 152° (analysis C). On adding hydrochloric acid to the alkaline extract and crystallizing the precipitate from alcohol, yellow prisms were obtained melting at about 113°. A nitrogen determination gave (analysis D):

	Calculated for $C_8H_{10}N_2OS$.	Found. C.	Found. D.
N	15.3	15.1	15.3

The ether extract contained the hydrazone,

$$C_6H_5NH{-}N{=}C{<}{\begin{matrix}OCH_3\\ SC_2H_5\end{matrix}},$$

which decomposed when an attempt was made to purify it by distillation under reduced pressure.

a-Benzoylphenylthioncarbazinicethyl Ester,

$$\begin{matrix}C_6H_5N{-}NHCS.OC_2H_5\\ |\\ C_6H_5CO\end{matrix}. —$$

When the thioncarbazinic ester is treated with benzoyl chloride, action begins about 90° and is complete on heating to 120° for a short time. On crystallizing from alcohol, fine colorless pyramids are obtained melting at 178°. This material is soluble in alkali, in which solution it can be boiled without decomposition. A nitrogen determination gave:

	Calculated for $C_{16}H_{16}N_2O_2S$.	Found.
N	9.3	9.3

The sodium salt of thioncarbazinicethyl ester was prepared by mixing the thion derivative with sodium alcoholate and evaporating in a vacuum. It forms a yellowish-red powder. When this was treated with benzoyl chloride, the above benzoyl compound was obtained.

Phenylhydrazone of Diethylthiocarbonic Ester,

$$C_6H_5NH{-}N{=}C{<}{\begin{matrix}OC_2H_5\\ SC_2H_5\end{matrix}}. —$$

As stated above, under the heading of phenylthioncarbazinicethyl ester, from 115 g. of xanthogenic ester and the

calculated quantity of phenylhydrazine, 37 g. of this hydrazone were obtained. In our first experiments with this substance, it was freed from the thion ester by shaking with alkali, and, after drying, it was distilled under reduced pressure. It was found that it invariably decomposed to some extent when treated in this way, although it boiled for the most part, at 190°–191° at 14 mm. pressure, and at 210°–213° at 36 mm. pressure. Thus obtained, it formed a thick yellowish-red oil which soon became dark-brown and resinous on exposure to the air. A nitrogen determination in a portion which had been distilled indicated that the substance obtained in this manner was not pure (analysis E).

It is better prepared from phenylthioncarbazinicethyl ester by treating the alcoholic solution with potash and ethyl iodide. Action takes place at ordinary temperature and, on filtering and evaporating, washing with water and drying over calcium chloride, it was found to distil at 198° at 20 mm. pressure. A nitrogen determination gave (analysis F):

	Calculated for $C_{11}H_{16}N_2OS$.	Found. E.	Found. F.
N	12.5	11.5	12.9

The alcoholic solution gives with ferric chloride a garnet-red solution. When hydrogen sulphide was led into this oil at a temperature of 125° for two hours and the material then allowed to cool, a mass of needles or prisms separated. The material was soluble in alkali and, on precipitating with hydrochloric acid and crystallizing from alcohol, fine needles melting at 73° were obtained. This material was, therefore, phenylthioncarbazinicethyl ester.

When hydrogen chloride is led into the hydrazone dissolved in ether or benzene, a colorless precipitate forms which rapidly deliquesces on exposure. On rapidly pressing it on paper, it was found to melt at about 57°, giving off ethyl chloride and leaving a residue of phenylthiolcarbazinicethyl ester.

Phenylhydrazone of Diethylthiocarbonic Ester and Thiobenzoic Acid. — 35 g. of the hydrazone were mixed with 20 g.

of thiobenzoic acid and warmed on the steam-bath for twelve hours. On cooling, the material partially solidified. It was filtered as far as possible on the pump, and the solid material was crystallized from alcohol, when prismatic crystals were obtained, melting constantly at 112°. These proved to be *phenylthiolcarbazinicethyl ester*. The oil filtered from this was distilled at 16 mm. pressure, whereupon it boiled mostly at 129°–131°. It was redistilled several times at ordinary pressure (760 mm.), and although it decomposed slightly by this treatment, it boiled constantly at 252°–253°. The boiling-point of *ethyl thiolbenzoate*, $C_6H_5CO.SC_2H_5$ is given by Engelhardt, Latschinoff, and Malyscheff * as 243° and by Seifert † as 241°–243°. In order to compare the above oil with ethyl thiolbenzoate, thiobenzoic acid, freshly prepared, was treated with alkali and ethyl bromide in alcohol, when action took place, on warming, and was complete in a few minutes. Water was then added and the oil taken up in ether, dried and distilled, when it practically all boiled over from 252° to 253°. On mixing this oil with the above, the boiling-point of the mixture was unaltered. The material was therefore ethyl thiolbenzoate, and the previous observations on the boiling-point of this ester are 10° too low, our observations being taken with an Anschütz thermometer.

Phenylhydrazone of Diethylthiocarbonic Ester and Benzoyl Chloride. — 5.7 g. of the hydrazone were mixed with 3.5 g. of benzoyl chloride in the cold, when the mixture became warm and effervesced, giving off ethyl chloride. On cooling, the material was crystallized from benzene and alcohol, when small lozenge-shaped crystals were obtained melting constantly at 138°–139°. It dissolves in alkali and is precipitated unaltered by acids, and a nitrogen determination gave:

	Calculated for $C_{16}H_{16}N_2O_2S$.	Found.
N	9.3	9.3

When this material is boiled with hydrochloric acid and alcohol, it slowly decomposes and goes into solution. On

* Zeitschr. Chem., 1868, 356. † J. prakt. Chem. [2], xxxi, 471.

adding sodium hydrate and crystallizing the precipitate thus produced, phenylthiolcarbazinicethyl ester melting at 112° is obtained. This same benzoyl derivative is formed when the thiolcarbazinic ester is warmed to 100° with benzoyl chloride. When it is heated with aniline, it gives carbanilide. This benzoyl derivative is in all probability *a-benzoylphenylthiolbazinicethyl ester*,

$$\begin{array}{l} C_6H_5\text{—N—NHCO.SC}_2H_5 \\ \quad\;\; | \\ C_6H_5CO \end{array}.$$

When the above hydrazone is diluted with benzene and acetyl chloride is added, a violent effervescence takes place. The product obtained after evaporation consists of a varnish which slowly solidifies. Beyond showing that it is readily soluble in alcohol and benzene it was not further examined. The hydrazone reacts with methyl iodide in the cold, and well-crystallized prisms separate. These will be investigated later, it being our intention to examine other hydrazones of the carbonic esters along similar lines.

Thioncarbanilicmethyl Ester, $C_6H_5NHCS.OCH_3$.—30 g. of phenyl mustard oil and 120 g. of methyl alcohol when boiled for twelve hours on the steam-bath, gave 29 g. of material melting at 95°–96°, after crystallizing from alcohol. This compound has recently been prepared by Orndorff and Richmond,* and they give its melting-point at 97°. A nitrogen determination gave:

	Calculated for C_8H_9NSO.	Found.
N	8.38	8.31

This substance gives a white precipitate with thallium hydrate which becomes black on boiling. When its alcohol solution was boiled with mercuric oxide, desulphurization took place slowly and, on concentrating the solution, carbanilide was obtained.

Thiolcarbanilicmethyl Ester, $C_6H_5NHCO.SCH_3$.—2 g. of the above compound were warmed with 2 g. of methyl iodide, and the product was crystallized from alcohol, when colorless

* Amer. Chem. Jour., xxii, 462.

plates were obtained melting at 81°–83°. This same compound was obtained when 5 g. of phenylthionethyl carbamate was heated on the steam-bath with 10 g. of methyl iodide. A nitrogen determination gave:

	Calculated for C_8H_9NSO.	Found.
N	8.38	8.44

This material gives a reddish-yellow precipitate with thallium hydrate which does not blacken on boiling (difference from the thion compound). It gives white precipitates with lead and silver nitrates, and it dissolves in concentrated sulphuric acid, and is precipitated out by water. It agrees therefore in properties with the compound obtained by Will * from phenylimidophenylthiocarbamicmethyl ester and sulphuric acid,

$$C_6H_5-NH-C=(NC_6H_5).SCH_3 + H_2O = C_6H_5NHCO.SCH_3 + H_2NC_6H_5.$$

Thioncarbanilicethyl Ester, $C_6H_5NHCS.OC_2H_5$, was prepared by boiling phenyl mustard oil with alcohol.† It was converted into *thiolcarbanilicethyl ester*, $C_6H_5NHCO.SC_2H_5$.—When 5 g. of thioncarbanilicethyl ester were heated for twelve hours with 15 g. of ethyl iodide on the steam-bath and the product crystallized from alcohol, a mass of colorless needles was obtained, melting at 71°–73°. This compound has already been prepared by Will by a different method.‡ When boiled with a mixture of alcohol and concentrated ammonia, it gave monophenylurea melting at 147°. Although this compound differs from the thion derivative by only about 1° in melting-point, when portions of each are mixed, the melting-point is lowered about 35°.

Thioncarbanilicisobutyl Ester, $C_6H_5NH-CS.OC_4H_9$.—Orndorff and Richmond state that heating isobutyl alcohol and phenyl mustard oil in sealed tubes at temperatures varying

* Ber. d. chem. Ges., xv, 341.

† Hofmann, Ber. d. chem. Ges., ii, 120; iii, 772; Liebermann, Ann. Chem. (Liebig), ccvii, 142; Orndorff and Richmond, Amer. Chem. Jour., xxii, 461.

‡ Loc. cit.

from 110° to 180° gave no solid product except thiocarbanilide. They prepared this substance by heating the materials for twenty hours on the water-bath, and state that it melts at 80.5°.

We found that, when 10 g. of phenyl mustard oil and 20 g. of isobutyl alcohol were heated in a closed tube for 115° to 125° for three hours, beautiful, long, colorless prisms were obtained which, after crystallization from alcohol, melted at 77° to 78°. A nitrogen determination gave:

	Calculated for $C_{11}H_{15}NSO$.	Found.
N	6.69	6.76

When 2.5 g. of the above compound were heated with 2.3 g. of isobutyl iodide in an oil-bath from 125° to 140°, no action whatever was observed.

Ethyl Thioncarbamate, $H_2NCSOC_2H_5$, *and Chloracetic Acid* were mixed in molecular proportions and heated on the steam-bath until ethyl chloride ceased being evolved. The mass was then pressed on a plate, taken up in ether and filtered. The ether was then evaporated and the residue extracted with benzene. On crystallizing the material from water and ether, it melted at 135° to 136° with effervescence. A nitrogen determination gave:

	Calculated for $H_2NCO.SCH_2COOH$.	Found.
N	10.37	10.20

This material is therefore carbaminthioglycollic acid, $H_2NCO.SCH_2COOH$. The yield was poor, as thioglycollic acid, thiolethyl carbamate, and cyanuric acid were also formed.

Isoamyl Thioncarbamate, $H_2NCSOC_5H_{11}$, *and Chloracetic Acid,* when heated on the steam-bath, deposited crystals which, when crystallized from ether, separated in the form of six-sided prisms melting at 123° to 125°. A nitrogen determination gave:

	Calculated for $C_3H_3NSO_2$.	Found.
N	11.96	11.65

This material is therefore the so-called mustard oil acetic acid, or *a-μ*-diketotetrahydrothiazole. This compound is formed far more readily by boiling the sulphocyanacetic esters with concentrated hydrochloric acid. It can be boiled under diminished pressure without decomposition. At 19 mm. pressure it boiled from 178.5° to 179.5°.

Silver a-μ-diketotetrahydrothiazole was prepared by precipitating the alkaline solution of the above compound with the calculated quantity of silver nitrate. It forms a light yellow powder which turns brown in the sunlight. A silver determination gave 49.8 per cent silver, instead of 48.2 per cent. Hydrogen sulphide regenerates the thiazole from this salt. The same result was obtained when it was treated with benzoyl chloride.

N-Methyl-a-μ-diketotetrahydrothiazole, $\left.\begin{matrix} S-CO \\ | \quad\quad \\ CH_2CO \end{matrix}\right> NCH_3$. — The above silver salt when suspended in ether and in benzene and heated for several days with methyl iodide, gave a product which boiled at 15 mm. pressure from 131° to 132°. This distillate solidified at once, on cooling, and when crystallized from benzene and ligroïn, melted from 37° to 39°. A nitrogen determination gave:

	Calculated for $C_4H_5NSO_2$.	Found.
N	10.6	10.5

For purposes of comparison *a-μ*-diketotetrahydrothiazole was methylated according to the method employed by Arapides,* when a product was obtained which boiled at 14 mm. pressure from 129° to 131° and was otherwise identical with the product from the silver salt. Arapides has shown that this product has the methyl group attached to nitrogen. He states that it forms an oil which slowly solidifies over sulphuric acid and that it very readily deliquesces. This is not the case when the material is purified by distillation; it then readily solidifies and does not deliquesce on exposure.

* Ann. Chem. (Liebig), ccxlix, 28.

When 1.4 g. of N-methyl-*α*-*μ*-diketotetrahydrothiazole, prepared either from the sodium or silver salt, was treated with 4.2 g. of sodium hydrate and 1.8 g. of silver nitrate added in aqueous solution, a gas was given off and a white gelatinous precipitate was obtained which turned yellow in the light. The gas was found to be carbon dioxide, and a silver determination in the precipitate gave 70.2 per cent, while the calculated percentage for silver thioglycollate $AgSCH_2COOAg$, is 70.5 per cent.

When this salt was decomposed with hydrogen sulphide, in aqueous solution, the filtrate gave with ferric chloride and ammonia the characteristic red-violet color of thioglycollic acid.

Thioncarbanilicethyl Ester, $C_6H_5NHCSOC_2H_5$, *and Chloracetic Acid* react on the steam-bath, giving off ethyl chloride and water, and not hydrochloric acid and alcohol. The product when crystallized from alcohol forms long colorless needles and melts from 147° to 148°, which is the melting-point of *n-phenyl-α-μ-diketotetrahydrothiazole* (Phenylsenfölglycolid), as found by Liebermann.* This reaction is much smoother than in the case of ethyl thioncarbamate and chloracetic acid.

Thioncarbanilicethyl Ester and α-Brompropionicethyl Ester (by G. K. Dustin).—When 18 g. of brompropionicethyl ester were heated with one molecular proportion of thioncarbanilicethyl ester for some time on the water-bath, then for a number of hours from 120° to 140°, a solid separated, on cooling. This crystallized from alcohol in groups of fine, colorless needles melting at 103°, and a nitrogen determination agreed with the calculated for

n-Phenyl-α-μ-diketo-β-methyltetrahydrothiazole,

$$\left.\begin{array}{r} S\text{—}CO \\ | \quad\;\; \\ CH_3CHCO \end{array}\right\rangle NC_6H_5:$$

	Calculated for $C_{10}H_9NO_2S$.	Found. I.	Found. II.
N	6.7	6.7	6.6

* Loc. cit.

Thioncarbanilicethyl Ester and a-Bromisobutyricethyl Ester, when heated for ten hours at 130°–155°, gave a solid, which, when crystallized from dilute alcohol, separated in the form of colorless prisms or pyramids and melted at 79°–81°. A nitrogen determination shows that this compound is *carbanil-α-thioisobutyricethyl ester*, $C_6H_5NHCO.SC(CH_3)_2CO_2C_2H_5$:

	Calculated for $C_{13}H_{17}SNO_3$.	Found.
N	5.2	4.9

This compound can be boiled with concentrated hydrochloric acid and recovered unaltered. When α-bromisobutyric acid and thioncarbanilicmethyl ester were heated as above, the only solid material isolated was aniline hydrobromide. This crystallized in plates which darkened at 245° and became black and melted with effervescence at about 280°. A bromine determination gave 46.2 per cent; calculated, 45.9 per cent.

The following sulphocyan derivatives of the fatty esters NCS—$CHRCO_2R'$, are obtained in good yields by boiling the corresponding α-halogen esters with potassium sulphocyanide in alcoholic solution. They are oils with a penetrating, persistent, and, for the most part, disagreeable odor. They can be distilled unaltered under reduced pressure.

The boiling-points which are given in the following experiments represent the temperatures at which the greater portion of the esters were collected. For the preparation of the sulphocyanides, in some cases, the bromesters were collected under wider limits than those given in the tables, the bromesters being freshly prepared from Kahlbaum's acids by the Hell-Volhard-Zelinsky method.

Experiments by Leeds Mitchell.

Methyl Sulphocyanacetate, $NCS.CH_2CO_2CH_3$.—75 g. of methyl chloracetate, 80 g. of absolute alcohol, and 60 g. of potassium sulphocyanide, after boiling twenty-four hours, gave 38 g. of methyl sulphocyanacetate, boiling from 120° to 122° at 16 mm. pressure.

Ethyl Sulphocyanacetate boiled at 118°–122° at 15 mm. pressure. Heintz,* who first prepared this ester, states that it boils in a vacuum at 180°–200°, and Claesson found that it boils with partial decomposition at 225° at ordinary pressure.

Isoamyl Sulphocyanacetate boiled at 145°–147° at 17 mm. pressure, while Claesson found that it boils at 255° at ordinary pressure.

α-μ-Diketotetrahydrothiazole (mustard-oil acetic acid, Senföllessigsäure), $\begin{matrix} CH_2CO \\ | \\ S{-}CO \end{matrix}\!\!>NH$. — 38 g. of methyl sulphocyanacetate and 76 g. of concentrated hydrochloric acid were boiled a few minutes until all the oil dissolved. The solution was then evaporated and the residue treated with benzene and filtered from ammonium chloride. The material dissolved by benzene was crystallized from water until it melted at 125°–126°. In this manner 2 g. of ammonium chloride and 20 g. of α-μ-diketotetrahydrothiazole were obtained. This product is identical in every respect with that obtained by heating isoamyl thioncarbamate with chloracetic acid as described above.

Experiments by Guy K. Dustin.

Methyl α-Sulphocyanpropionate, $CH_3{-}CH.SCN.CO_2CH_3$. — This was prepared by boiling 57 g. of methyl α-brompropionate with one molecular proportion of potassium sulphocyanide and twice its weight of alcohol until a test with ferric chloride showed no potassium sulphocyanide. This required ten hours. After filtering and evaporating the alcohol, practically the entire product boiled at 104°–106° at 15–16 mm. pressure. The yield obtained was 34 g., while the calculated yield is 46 g.

Nitrogen determinations gave the following results:

	Calculated for $C_5H_7NSO_2$.	Found. I.	Found. II.
N	9.65	10.1	10.2

The material was obtained as a colorless oil with a strong, peculiar, but not unpleasant, odor.

* Loc. cit.

Ethyl α-Sulphocyanpropionate. — When 30 g. of ethyl α-brompropionate were boiled with one molecular proportion of potassium sulphocyanide, it required two days before the action was complete. On distilling the reaction-product at 16 mm. pressure it all boiled at 104°–110°, mostly at 107°–108°. The yield was 22 g., and an analysis of the colorless oil thus obtained gave:

	Calculated for $C_6H_9NSO_2$.	Found.
N	8.8	8.9

Isobutyl α-Sulphocyanpropionate was obtained when 71 g. of isobutyl α-brompropionate was boiled in alcoholic solution with 33 g. of potassium sulphocyanide. On distilling at 15 mm. pressure, 38 g. of clear, colorless oil, boiling at 130°–131° were collected, the odor of which was not unpleasant. A nitrogen determination gave:

	Calculated for $C_8H_{13}NSO_2$.	Found.
N	7.48	7.48

Isoamyl α-Sulphocyanpropionate was prepared by boiling 87 g. of the bromester with potassium sulphocyanide and alcohol for seven hours. It boiled at 141.5° at 15 mm. pressure, and the yield was 67 g. It was thus obtained as a colorless oil, the odor of which was not unpleasant. A nitrogen determination gave:

	Calculated for $C_9H_{15}NSO_2$.	Found.
N	6.9	7.0

When this oil is distilled at ordinary pressure, it boils with decomposition at 265°–267°.

The boiling-points of the α-brompropionic esters used in making the above sulphocyan derivatives were as follows:

The *methyl ester* boiled at 51.5° at 19 mm. pressure.

The *ethyl ester* boiled at 56°–58° at 14 mm. pressure.

The *isobutyl ester* boiled at 79°–80° at 14 mm. pressure.

The *isoamyl ester* boiled at 99°–100° at 16 mm. pressure.

β-Methyl α-μ-Diketotetrahydrothiazole,

$$\begin{array}{l} CH_3.CH\text{—}CO \\ \quad | \qquad\qquad >NH. \\ S\text{———}CO \end{array}$$

— The best yield of this substance was obtained from the methyl ester. 11 g. of methyl *α*-sulphocyanpropionate and 15 g. of concentrated hydrochloric acid were mixed and evaporated to dryness on the steam-bath. Benzene then removed 0.6 g. of ammonium chloride, and 7.8 g. of crude thiazole were obtained. This, when crystallized from a mixture of benzene and ligroïn, separated in the form of colorless leaves and melted at 46°–47°, and nitrogen determinations gave the following:

	Calculated for $C_4H_5NSO_2$.	Found. I.	Found. II.
N	10.6	10.5	10.5

On distilling it at 20 mm. pressure it boiled, for the most part, from 165° to 168°. Silver nitrate added to the alkaline solution of this substance produces a bulky, white, but not gelatinous, precipitate of the silver salt. It is decomposed by warm water.

Experiments by Harry LeB. Gray.

Methyl α-Sulphocyanisobutyrate, $(CH_3)_2C.SCN.CO_2.CH_3$, was obtained in a similar manner to the preceding sulphocyanides as a heavy, colorless oil having a disagreeable, penetrating odor. It boiled for the most part from 101° to 102° at 17 mm. pressure. This fraction was analyzed with the following result:

	Calculated for $C_6H_9NSO_2$.	Found.
N	8.8	8.9

Ethyl α-Sulphocyanisobutyrate resembles the methyl ester in properties. The greater portion boiled at 111°–115° at 22 mm. pressure. A nitrogen determination gave:

	Calculated for $C_7H_{11}NSO_2$.	Found.
N	8.09	8.68

Isobutyl α-Sulphocyanisobutyrate.— The product in this case,

after several distillations, boiled at 132°–133° at 21 mm. pressure. This fraction gave the following result on analysis:

	Calculated for $C_9H_{15}NSO_2$.	Found.
N	6.96	6.90

Isoamyl a-Sulphocyanisobutyrate, on fractioning, boiled at 185.5°–186.5° at 16 mm. pressure. A nitrogen determination gave:

	Calculated for $C_{10}H_{17}NSO_2$.	Found.
N	6.5	7.1

This material, like the preceding, is a colorless oil with a penetrating, disagreeable odor.

The boiling-points of the *a*-bromisobutyric esters used in making the above sulphocyan derivatives were as follows:

The *methyl ester* boiled at 51°–52° at 19 mm. pressure.
The *ethyl ester* boiled at 70°–71° at 20 mm. pressure.
The *isobutyl ester* boiled at 83°–85° at 16 mm. pressure.
The *isoamyl ester* boiled at 107°–108° at 25 mm. pressure.

β-Dimethyl a-μ-Diketotetrahydrothiazole,

$$\begin{array}{l} (CH_3)_2C{-}CO\diagdown \\ \quad\ |\qquad\qquad\quad\ \ NH.— \\ \quad\ S{-}CO\diagup \end{array}$$

The best yield of this substance was obtained from the methyl ester; the amyl ester failed to give the compound. 14 g. of methyl *a*-sulphocyanisobutyrate were mixed with 20 c. c. concentrated hydrochloric acid and heated on the steam-bath for about one hour. The reaction is complete when no more oil remains on the surface of the liquid. The solution, when evaporated, gave 1 g. of ammonium chloride, the remaining material being the thiazole derivative. This crystallizes from water in enormously lengthened, colored prisms, one crystal being obtained that measured 31 mm. long and 1.5 mm. in diameter. It melts at 79°–80°, and a nitrogen determination gave:

	Calculated for $C_5H_7NSO_2$.	Found.
N	9.65	9.87

Experiments by Henry A. North.

Methyl α-Sulphocyanbutyrate, $C_2H_5CH.SCN.CO_2CH_3$.—This was obtained as a colorless oil boiling at 125° at 28 mm. pressure, and a nitrogen determination gave the following result:

	Calculated for $C_6H_9NSO_2$.	Found.
N	8.8	8.6

Ethyl α-Sulphocyanbutyrate.—On mixing 100 g. of the bromester, 49.6 g. of potassium sulphocyanide, and 200 c. c. of alcohol, and boiling for twelve hours, somewhat more than 65 g. of a clear, colorless oil was obtained. This boiled from 134° to 136° at 28 mm. pressure. Like the other members of this series, it has a strong, unpleasant, extremely persistent odor. A nitrogen determination gave the following result:

	Calculated for $C_7H_{11}NSO_2$.	Found.
N	8.09	8.35

Isoamyl α-Sulphocyanbutyrate was obtained as a colorless oil which, after fractionation, boiled from 158° to 160° at 23 mm. pressure. A nitrogen determination gave:

	Calculated for $C_{10}H_{17}NSO_2$.	Found.
N	6.51	6.37

The boiling-points of the α-brom normal butyric esters used in making the above sulphocyan derivatives were as follows:

The *methyl ester* boiled at 67°–72° at 25 mm. pressure.

The *ethyl ester* boiled at 68°–69° at 19 mm. pressure.

The *iosamyl ester* boiled at 110.5°–113.5° at 19 mm. pressure.

β-Ethyl α-μ-Diketotetrahydrothiazole, $C_2H_5CH\begin{array}{l}—CO\diagdown \\ \diagdown S—CO\diagup\end{array}NH.$—

This is best obtained from the methyl or ethyl esters. On warming these with concentrated hydrochloric acid, until solution took place and then evaporating, a colorless oil was

obtained which solidified on cooling. When crystallized from a mixture of benzene and ligroïn, six-sided prisms separated which finally melted from 63° to 65°, and a nitrogen determination gave the following result:

	Calculated for $C_5H_7NSO_2$.	Found.
N	9.65	9.68

Experiments by W. H. Buell.

Methyl a-Sulphocyanisovalerianate, $(CH_3)_2CH{-}CH.SCN.CO_2CH_3$. — 39 g. of the bromester, 78 g. of alcohol, and 19.4 g. of potassium sulphocyanide, warmed on the water-bath for two days, gave 14 g. of colorless oil boiling from 119° to 121.5° at 23 mm. pressure. It has a peculiar penetrating unpleasant odor. A nitrogen determination gave:

	Calculated for $C_7H_{11}NSO_2$.	Found.
N	8.09	8.35

Ethyl a-Sulphocyanisovalerianate. — 88 g. of the bromester, 40.8 g. of potassium sulphocyanide and 176 g. of alcohol were boiled for three days. On fractioning, 84 g. of ester were obtained, boiling from 126° to 128° at 19 mm. pressure. This was analyzed with the following result:

	Calculated for $C_8H_{13}NSO_2$.	Found.
N	7.48	7.85

Isobutyl a-Sulphocyanisovalerianate. — 55 g. of the bromester, 22.5 g. of potassium sulphocyanide and 110 g. of alcohol gave 19 g. of oil, boiling, for the most part, from 145° to 147° at 19 mm. pressure. This gave the following result on analysis:

	Calculated for $C_{10}H_{17}NSO_2$.	Found.
N	6.5	5.8

This ester, like the above, had a strong, peculiar odor which, perhaps, was not unpleasant.

Isoamyl a-Sulphocyanisovalerianate. — 105 g. of the brom-

ester, 210 g. of alcohol and 40.6 g. of potassium sulphocyanide gave a colorless oil with a disagreeable odor after boiling for two days. The greater portion of this boiled from 151° to 152° to 14 mm. pressure and a nitrogen determination gave the following result:

	Calculated for $C_{11}H_{19}NSO_2$.	Found.
N	6.11	6.32

The boiling-points of the *a*-bromisovalerianic esters used in making the above sulphocyan derivatives were as follows:

The *methyl ester* boiled at 174°–182° at 760 mm. pressure.

The *ethyl ester* boiled at 186°–187° at 764 mm. pressure.

The *isobutyl ester* boiled at 105°–108° at 17 mm. pressure.

The *isoamyl ester* boiled at 113°–114° at 16 mm. pressure.

When the above sulphocyanic esters were boiled with hydrochloric acid, the products were oils in each case. The ethyl ester gave a product which solidified in a freezing-mixture, but, on attempting to crystallize it, or on removing it from the freezing-mixture, it became liquid, and, on attempting to distil it under diminished pressure, it decomposed.

For convenience of reference, the boiling-points of the sulphocyanic esters, described by us, are collected in the following table:

	Pressure in mm.	Boiling-point.
Methyl a-Sulphocyanacetate	16	120°–122°
Ethyl "	15	118°–122°
Isoamyl "	17	145°–147°
Methyl a-Sulphocyanpropionate	15–16	104°–106°
Ethyl "	16	107°–108°
Isobutyl "	15	130°–131°
Isoamyl "	15	141-5°
Methyl a-Sulphocyanisobutyrate	17	101°–102°
Ethyl "	22	111°–115°
Isobutyl "	21	132°–133°
Isoamyl "	16	135.5°–136.5°
Methyl a-Sulphocyanbutyrate	23	125°
Ethyl "	28	134°–136°

	Pressure in mm.	Boiling-point.
Isoamyl α-Sulphocyanbutyrate	23	158°–160°
Methyl α-Sulphocyanisovalerianate	23	119°–121.5°
Ethyl "	19	126°–128°
Isobutyl "	19	145°–147°
Isoamyl "	14	151°–152°

New Haven, April 3, 1900.

ON UREAIMIDO-ESTERS, THIOUREAIMIDO-ESTERS, ACYLTHIOUREAIMIDO-ESTERS, AND UREAAMIDINES.*

[PRELIMINARY PAPER.]

BY HENRY L. WHEELER AND W. MURRAY SANDERS.

REPRESENTATIVES of new classes of compounds, isomeric or metameric with the acylpseudourea ethers, acylpseudothiourea ethers, and diacylpseudothiourea ethers, can be prepared by combining isocyanates, mustard oils, and acyl rhodanides with imido-esters. The imido-esters immediately combine with phenyl isocyanate, at ordinary temperatures, giving a quantitative yield of an addition-product as follows:

$$C_6H_5C\left\langle\begin{matrix}NH\\ OR\end{matrix}\right. + CONC_6H_5 = C_6H_5C\left\langle\begin{matrix}NCONHC_6H_5\\ OR\end{matrix}\right. .$$

This class of compounds, perhaps, may be called ureaimido-esters or carbamidimido-esters, since they have the structure of imido-esters and ureas combined. They are extremely sensitive towards hydrogen chloride, by which reagent, just as the acylpseudourea ethers † (II) they are readily and quantitatively converted in the cold, with loss of alkyl chloride, into acylureas. This reaction with these two classes of compounds proceeds as follows:

$$\begin{array}{ccc}
\text{I.} & & \text{II.} \\
C_6H_5C{=}NCONHC_6H_5 & & C_6H_5CON{=}C{-}NHC_6H_5 \\
\diagdown OR & & \diagdown OR \\
+\ HCl - RCl & & +\ HCl - RCl \\
& \rightarrow C_6H_5CONHCONHC_6H_5 \leftarrow &
\end{array}$$

It will be noticed that the imido-ester groupings in the different positions in these isomers are affected alike, inasmuch

* Jour. Amer. Chem. Soc., xxii, No. 7.
† Stieglitz and Dains, Ibid., xxi, 136.

as under similar conditions both compounds give with hydrogen chloride the same derivative, benzoylphenylurea. The urea-imido-esters (I) readily react with aniline, at the temperature of the steam-bath, and ureaamidines are formed as follows:

III.

$$C_6H_5C\left\langle\begin{array}{l}NCONHC_6H_5\\ OR\end{array}\right. + H_2NC_6H_5 = C_6H_5C\left\langle\begin{array}{l}NCONHC_6H_5\\ NHC_6H_5\end{array}\right. + ROH.$$

Whether the structure shown in formula III or the tautomeric form is to be assigned to these amidines must be decided later. These amidines have little or no basic properties.

The mustard oils, phenyl mustard oil and allyl mustard oil, react less energetically than phenyl isocyanate with the imido-esters. On long standing or on warming, the mixtures deposit crystals. These compounds, for which the name thioureaimido-esters (IV) is proposed, are closely similar to the above oxygen analogues, since with hydrogen chloride, under similar conditions, they readily separate alkyl chloride and give the corresponding acylthioureas. The mechanism of the reaction is as follows:

IV.

$$C_6H_5C\left\langle\begin{array}{l}NCSNHC_6H_5\\ OR\end{array}\right. \rightarrow C_6H_5C\left\langle\begin{array}{l}NHCSNHC_6H_5\\ Cl\\ OR\end{array}\right.$$

$$\rightarrow C_6H_5CONHCSNHC_6H_5 + RCl.$$

The isomeric acylpseudothiourea ethers and the diacylpseudothiourea ethers apparently have not yet been prepared, so that a comparison of the behavior of these compounds with the thioureaimido-ester derivatives must be deferred to a later date.

When the thioureaimido-esters are warmed with aniline, and other organic bases, thioureas are formed. The imido-esters combine with acetyl and benzoyl thiocyanates with evolution of heat, the mixtures readily solidifying. Acylthioureaimido esters (V) are then produced, as follows:

V.

$$C_6H_5C\begin{matrix}\diagup NH \\ \diagdown OR\end{matrix} + CSN.COC_6H_5 = C_6H_5C\begin{matrix}\diagup NCSNH.COC_6H_5 \\ \diagdown OR\end{matrix}$$

These compounds are formed more readily than the above, and they are far more unstable than the thioureaimido-esters. When they are warmed with hydrochloric acid, they decompose in a different manner from the other types of ureaimido-esters. A monoacylthiourea, and not a diacyl derivative, is obtained. The decomposition under this treatment takes place at the double union as follows:

VI.

$$C_6H_5C\begin{matrix}\diagup NCSNHCOC_6H_5 \\ \diagdown OR\end{matrix} + H_2O = C_6H_5C\begin{matrix}\diagup O \\ \diagdown OR\end{matrix} + H_2NCSNHCOC_6H_5.$$

What appears to be the nearest known analogue to a metamer of the above or dibenzoylpseudothiourea ether is the ethylisodicarbethoxyurea, $C_2H_5O.CON{=}C{<}\begin{matrix}NCO.OC_2H_5 \\ OC_2H_5\end{matrix}$, of Dains.* This compound is also very sensitive towards hydrogen chloride; however, it does not separate at the double union, like the above, but decomposes with the evolution of ethyl chloride, giving the diacylurea, $C_2H_5OCONHCONHCO.OC_2H_5$. The ease with which the ureaimido esters decompose with hydrochloric acid, without forming a stable intermediate addition product or "salt," recalls the perfectly analogous behavior of the acylimido-esters.† In the case of the latter, the above two reactions with hydrogen chloride were also observed. The properties of the ureaimido-esters, in general, approach more nearly to those of the acylimido-esters than to those of other types of imido-esters.

When the acylthioureaimido-esters are treated with aniline, toluidine, etc., thioureas are formed.

The action of phenylhydrazine on the acylthioureaimido esters seemed theoretically promising for the preparation of

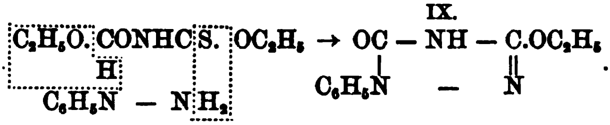
* Loc. cit.

† Wheeler, Walden and Metcalf, Amer. Chem. Jour., xix, 129 and xx, 64.

triazole derivatives; but it appears, from preliminary experiments, that, although hydrogen sulphide is evolved in this treatment, triazoles do not result, at least not as the chief product. The hydrogen sulphide, first formed, decomposes a part of the ureaimido ester, giving benzoylthiourea, etc.

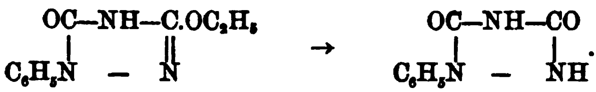
Experiments in this laboratory by Dr. Bayard Barnes have shown that the acylphenylthioureas react with aniline and phenylhydrazine with the removal of the acyl group. With phenylhydrazine no triazole derivative was obtained. Similar results were obtained with the acylphenylurethanes, acetylphenylurethane, formylphenylurethane,* and acetylphenylthiourethane. It is probable that other diacylanilides will be found to act similarly. On the other hand, those acylurethanes which do not contain a phenyl group such as acetylurethane,† acetyl- and benzoylthionurethane, give triazole derivatives. Dr. Barnes has also found that carbethoxythionurethane of Delitsch ‡ readily reacts with phenylhydrazine as follows:

IX.



That the compound formed in this reaction is 1-phenyl-3-ethoxy-5-triazolon, and that it has the structure represented by formula IX, is shown by its behavior on boiling with strong hydrochloric acid, whereupon it is converted into Pinner's § urazole, (X):

X.



The process which in general serves for the preparation of simple or monosubstituted ureas and thioureas, and which consists of treating a salt of an amine with potassium cyanate or thiocyanate, does not lead to the formation of the prototypes

* Wheeler and Metcalf, Amer. Chem. Jour., xix, 217.

† Andreocci, Ber. d. chem. Ges., xxii, R. 737; Ibid., xxiv, R., 203.

‡ J. prakt. Chem., x, 118.

§ Ber. d. chem. Ges., xxi, 1219.

of the above urea derivatives, when applied to the salts of the imido-esters. This fact seems to the writer to be a strong argument in support of the theory of Stieglitz that the salts of the imido-esters are not ammonium derivatives, but that they are derived from the form $\mathrm{RC}\begin{matrix}\diagup\mathrm{NH_2}\\ -\mathrm{Cl}\\ \diagdown\mathrm{OR}\end{matrix}$, etc. In fact, the properties of the cyanic and thiocyanic acid salts do not agree with those which would be expected for salts having an ammonium structure.

When ice-cold solutions of benzimidoisobutyl ester hydrochloride and potassium cyanate, in molecular proportions, are mixed together, a mass of well-crystallized, colorless prisms separates. If an attempt is made to filter these at ordinary temperature, they rapidly decompose, giving off a gas (CO_2) and completely liquefying. Owing to the unstable nature of this salt, which is undoubtedly a cyanate, it was not examined further. On the other hand, the corresponding thiocyanic salt is far more stable. It can be prepared, at ordinary temperature, by mixing solutions of the imido-ester hydrochloride with potassium thiocyanate, whereupon a bulky mass of colorless prisms or needles separates. This salt has the structure represented by formula XI, and all attempts to rearrange it into the metameric thioureaimido ester (XII) failed.

$$\text{XI.}\quad \mathrm{C_6H_5C}\begin{matrix}\diagup\mathrm{NH_2}\\ -\mathrm{SCN}\\ \diagdown\mathrm{OC_4H_9}\end{matrix} \qquad\qquad \text{XII.}\quad \mathrm{C_6H_5C}\begin{matrix}/\!\!/\mathrm{NCSNH_2}\\ \\ \diagdown\mathrm{OC_4H_9}\end{matrix}$$

When this salt is warmed in aqueous solution, it dissolves, but the solution almost immediately becomes turbid and an oil (isobutyl benzoate) separates. On evaporating to dryness, nothing but ammonium thiocyanate is obtained. The decomposition then proceeds as follows:

$$\mathrm{C_6H_5C}\begin{matrix}\diagup\mathrm{NH_2}\\ -\mathrm{SCN}\\ \diagdown\mathrm{OC_4H_9}\end{matrix} + \mathrm{H_2O} = \mathrm{C_6H_5CO.OC_4H_9} + \mathrm{NH_4SCN}.$$

If the dry salt is heated above its melting-point, it decomposes smoothly as follows:

$$C_6H_5C\begin{cases}NH_2\\ SCN\\ OC_4H_9\end{cases} \rightarrow C_6H_5CO.NH_2 + C_4H_9SCN.$$

It will be noticed that these reactions are analogous in every respect to those of the hydrochloric acid salts of the imido-esters.

Experimental Part.

Phenylureaimidoisobutyl Benzoate, $C_6H_5C\begin{matrix}\diagup\!\!\!\diagup NCONHC_6H_5\\ \diagdown OC_4H_9\end{matrix}$.— Phenyl isocyanate (3.4 g.) and benzimidoisobutyl ester (10 g.) combined with evolution of heat, and the mixture solidified to a white mass. When this was crystallized from alcohol, colorless prisms were obtained which melted from 99° to 100°. A nitrogen determination gave:

	Calculated for $C_{18}H_{20}N_2O_2$.	Found.
N	9.4	9.1

Action with Hydrogen Chloride. — Some of the above material was dissolved in benzene, and the solution was saturated with hydrogen chloride, whereupon colorless prisms separated, melting at about 200°. This material proved to be *Benzoylphenylurea*, $C_6H_5CONHCONHC_6H_5$, which crystallized from alcohol in long silky needles, and on boiling it with sodium hydroxide it gave phenylurea.

The extreme sensitiveness of compounds of this type toward hydrochloric acid was shown by the fact that it was found to be impossible to isolate ureaimido-esters from benzimidomethyl, ethyl, and phenylacetimidomethyl esters and phenyl isocyanate, if the latter contained phosphorus oxychloride. Under these conditions the benzimido-esters gave *benzoylphenylurea*, while phenylacetimidomethyl ester gave a compound very difficultly soluble in alcohol. It crystallized in the form of needles and melted at 166°, and a nitrogen

determination showed that it was *phenylacetylphenylurea*, $C_6H_5CH_2CONHCONHC_6H_5$:

	Calculated for $C_{15}H_{14}N_2O_2$.	Found.
N	11.0	11.0

Action with Aniline.—Phenylureaimidoisobutyl benzoate (2 g.) and aniline (0.6 g.) were mixed in benzene and warmed on the water-bath, whereupon a substance separated in granular crystals. It was found to be very difficultly soluble in alcohol (a property of ureaamidines which is general as far as we have observed), and on boiling with alcohol it melted at 179°–180°. A nitrogen determination agreed with the figures calculated for *benzenylphenylureaphenylamidine*, $C_6H_5NH-(C_6H_5)C{=}NCONHC_6H_5$.

	Calculated for $C_{20}H_{17}N_3O$.	Found.
N	13.3	13.0

This amidine is insoluble in dilute hydrochloric acid, and no hydrochloric acid salt was obtained when the material was dissolved in benzene and saturated with hydrogen chloride. It is insoluble in alkali.

Phenylthioureaimidomethyl Benzoate, $C_6H_5C\begin{cases}{=}NCSNHC_6H_5.\\ -OCH_3\end{cases}$—Equal quantities of benzimidomethyl ester and phenyl mustard oil (5 g. of each) were mixed and kept at a temperature of about 60°–70° for two days. On cooling, then, the mixture solidified almost completely. In each of the experiments with phenyl mustard oil and the imido-esters, a yellow mixture resulted, although the ingredients before mixing were colorless. On crystallizing from alcohol, beautiful colorless or cream-colored lozenge-shaped tables were obtained which melted sharply at 132°. The material is readily soluble in benzene and hot alcohol, difficultly in cold alcohol, and a nitrogen determination gave:

	Calculated for $C_{15}H_{14}N_2OS$.	Found.
N	10.37	10.29

When this compound was treated with cold dilute hydrochloric acid, in which it is insoluble, little or no action was observed after two days' standing. When a little alcohol was added and the whole was warmed, effervescence took place, methyl chloride was evolved, and, on cooling, the long characteristic colorless needles of *benzoylphenylthiourea*, C_6H_5CO $NHCSNHC_6H_5$, were obtained, melting at about 148°.

Phenylthioureaimidoethyl Benzoate, $C_6H_5C\begin{matrix}/\!\!/ NCSNHC_6H_5 \\ \diagdown OC_2H_5\end{matrix}$. — Benzimidoethylester (5 g.) and phenyl mustard oil (4.5 g.) gave a yellow oil directly on mixing. After two days the material solidified to a glistening mass of flattened prisms or tables, and on crystallizing from alcohol it separated in the form of cream-colored tables, and it melted sharply at 119°. These thioureaimido esters, in general, show a great tendency to crystallize. A nitrogen determination gave:

	Calculated for $C_{16}H_{16}N_2OS$.	Found.
N	9.8	9.7

When treated with hydrochloric acid, it behaved precisely like the methyl ester, and benzoylphenylthiourea was obtained.

Phenylthioureaisobutyl Benzoate, $C_6H_5C\begin{matrix}/\!\!/ NCSNHC_6H_5 \\ \diagdown OC_4H_9\end{matrix}$. — Benzimidoisobutyl ester (5 g.) and phenyl mustard oil (3.8 g.) behaved, on mixing and standing, precisely like the above. When crystallized from alcohol, it forms large, stout tables, and it melts at 125°. A nitrogen determination gave:

	Calculated for $C_{18}H_{20}N_2OS$.	Found.
N	8.9	8.9

When this was treated with hydrochloric acid and warmed, *benzoylphenylthiourea* was obtained.

When 2 g. of this imido-ester were warmed on the water-bath with aqueous-alcoholic ammonia for a number of hours and then allowed to cool, colorless crystals separated, melting at 151°–153°. A nitrogen determination gave 18.5 per

cent, while the calculated for benzenylphenylthiourea amidine is 27.0 per cent, and that for phenylthiourea, which melts at 154°, is 18.4 per cent. The material, in fact, had the bitter taste and other properties of *phenylthiourea*.

When this thioureaimido-ester was treated with methyl iodide, a varnish was obtained which crystallized after long standing.

Phenylthioureaisobutyl benzoate readily reacts with phenyl hydrazine, giving off hydrogen sulphide, and it gives a compound which crystallizes in plates when treated with benzoyl chloride. These reactions will receive more thorough attention later.

Acetylthioureaimidoisobutyl Benzoate,

$$C_6H_5C\begin{matrix}\nearrow NCSNHCOCH_3 \\ \searrow OC_4H_9\end{matrix}.—$$

Benzimidoisobutyl ester and acetyl thiocyanate combine with evolution of considerable heat and, on cooling, the mixture completely solidifies, whereupon, on crystallizing from alcohol, colorless needles are obtained which melt at 125°–126°. A nitrogen determination gave:

	Calculated for $C_{14}H_{18}N_2O_2S$.	Found.
N	10.0	9.9

When this imido-ester was treated in alcoholic solution with hydrogen chloride, a compound was obtained, melting at 166°, which had all the properties of *acetylthiourea*, $CH_3CONHCSNH_2$.

With phenylhydrazine it evolves hydrogen sulphide, and on crystallizing the product from alcohol acetylthiourea separates.

Benzoylthioureaimidoethyl Benzoate,

$$C_6H_5C\begin{matrix}\nearrow NCSNHCOC_6H_5 \\ \searrow OC_2H_5\end{matrix}.—$$

When benzimidoethyl ester (6.1 g.) was mixed with 5.6 g. of benzoyl sulphocyanate, the mixture completely solidified. On crystallizing from alcohol, needles were obtained which melted at 131°–132°, and on analysis the following result was obtained:

	Calculated for $C_{17}H_{16}N_2O_2S$.	Found.
N	8.9	8.8

When this imido-ester was warmed with phenylhydrazine, the only crystalline material obtained was *benzoylthiourea.*

Benzoylthioureaimidoisobutyl Benzoate,

$$C_6H_5C\begin{cases}{/\!\!/}NCSNHCOC_6H_5\\ \diagdown OC_4H_9\end{cases}.—$$

When benzimidoisobutyl ester (10 g.) and benzoyl sulphocyanate (7.4 g.) were mixed, considerable heat was evolved and the mass solidified. When this was crystallized from alcohol, colorless needles, melting at 120°, were obtained. A nitrogen determination gave:

	Calculated for $C_{19}H_{20}N_2O_2S$.	Found.
N	8.2	8.4

When this imido-ester was treated with hydrogen chloride in benzene solution, *benzoylthiourea*, melting at 169°–170°, was obtained. Apparently this same compound was obtained when the ester was treated with ammonia, phenylhydrazine, and with benzoyl chloride. These results show the great tendency this ester has to separate at the double bond.

Benzoylthioureaimidoisobutyl Benzoate Methyl Iodide,

$$C_6H_5C\begin{cases}{/\!\!/}NCSNHCOC_6H_5\\ \quad CH_3I\\ \diagdown OC_4H_9\end{cases}.—$$

The above imido-ester and methyl iodide combine in benzene solution to form a compound containing iodine and which crystallizes from alcohol in well-developed, colorless prisms melting at 204°–205°. A nitrogen determination gave:

	Calculated for $C_{20}H_{23}N_2O_2SI$.	Found.
N	5.7	5.7

Benzoylthioureaimidomethylphenyl Acetate,

$$C_6H_5CH_2C\begin{cases}{/\!\!/}NCSNHCOC_6H_5\\ \diagdown OCH_3\end{cases}.—$$

When phenylacetimidomethyl ester (5.6 g.) was treated with

benzoylthiocyanate (5 g.), the mixture solidified immediately. It was crystallized from alcohol, and obtained in the form of colorless needles melting at 116°–117°. A nitrogen determination gave:

	Calculated for $C_{17}H_{18}N_2O_2S$.	Found.
N	8.9	9.3

When this imido-ester was treated with phenylhydrazine, hydrogen sulphide was evolved, but the product, on crystallizing from alcohol, was neither an amidine nor a triazole. It contained 15.4 per cent of nitrogen, while the calculated for *benzoylthiourea* is 15.5 per cent. It agreed in all its properties with the acylthiourea.

Benzoylthioureaimidoethylphenyl Acetate,

$$C_6H_5CH_2C\begin{matrix}\nearrow NCSNHCOC_6H_5\\ \searrow OC_2H_5\end{matrix},$$

was prepared from phenylacetimidoethyl ester. It forms colorless needles from alcohol which melt from 140° to 141°. When treated with hydrogen chloride in alcoholic solution, it gave small prismatic crystals, melting at 169°–170°, and a nitrogen determination agreed with the calculated for benzoylthiourea:

	Calculated for $C_8H_8N_2SO$.	Found.
N	15.5	15.6

The Thiocyanic Acid Salt of Benzimidoisobutyl Ester,

$$C_6H_5C\begin{matrix}\nearrow NH_2\\ -SCN\\ \searrow OC_4H_9\end{matrix},$$

is readily formed on mixing aqueous solutions of the imido-ester hydrochloride and potassium cyanate. It then separates as a mass of colorless needles or prisms which are quite difficultly soluble in water. It melts at about 130°. A portion dried in a desiccator over calcium chloride and then for a few minutes at 60°–70° gave the following results on analysis:

	Calculated for $C_{12}H_{16}N_2SO$.	Found.
N	11.8	11.9

Its reaction with iron chloride and with alkali showed that this material was a salt of the imido-ester and not the isomeric thioureaimidoisobutyl benzoate. It decomposes on warming with water, smoothly, into ammonium thiocyanate and isobutyl benzoate, and when heated above its melting-point it gives benzamide and isobutyl thiocyanate.

Experiments by Bayard Barnes.

Carbethoxythioncarbamic Ester, $C_2H_5OCONHCS.OC_2H_5$.— This was prepared according to the directions of Delitsch;* when purified by means of its potassium salt, it was found to boil unaltered at 135° at 18 mm. pressure. It melts at 44°.

1-Phenyl-3-ethoxy-5-triazolone, $\begin{array}{l} \qquad\quad OC—NH—C.OC_2H_5 \\ \qquad\qquad\diagdown\qquad\diagup\!\!\diagup \\ C_6H_5N—N \end{array}$, was obtained when the above carbamic ester (15 g.) was heated with phenylhydrazine (9 g.) on the steam-bath. After the evolution of hydrogen sulphide and alcohol had ceased, the material was crystallized from hot water, whereupon colorless needles, melting at 150°–151°, were obtained. This material was soluble in alkali and was precipitated unaltered by acids. It contained no sulphur, and on analysis the following results were obtained:

	Calculated for $C_{10}H_{11}N_3O_2$.	Found.
C	58.5	58.9
H	5.2	5.3
N	20.5	20.4

When this compound was boiled for some time with concentrated hydrochloric acid and alcohol, colorless plates were obtained, which melted at 263°, showing signs of melting at 255°. For purposes of comparison Pinner's † urazole was prepared, and it was found to be identical with the above.

Acetylphenylurethane, $CH_3CO(C_6H_5)NCO.OC_2H_5$.—10 g. of phenylurethane were boiled with an equal weight of acetic anhydride for several hours, whereupon, on pouring into water, unaltered urethane was obtained. Acetyl chloride was then

* J. prakt. Chem., x, 118.

† Loc. cit.

added and boiled for about one hour. Then about one-half of the solution was distilled off at ordinary pressure, and the remainder at 10 mm. pressure, whereupon the material practically all boiled at 142°–143°. It was thus obtained as a colorless oil which, like formylphenylurethane, refused to solidify on cooling. A nitrogen determination gave:

	Calculated for $C_{11}H_{13}NO_3$.	Found.
N	6.7	7.3

When this compound was gently warmed with phenylhydrazine and the product was crystallized from benzene, colorless plates, melting at 128°, were obtained. The following nitrogen determination showed that this material was not a triazole derivative, but rather *acetylphenylhydrazine*:

	Calculated for $C_8H_{10}N_2O$.	Found.
N	18.6	18.0

The action of phenylhydrazine on Hugershoff's* *acetylphenylthiocarbamide*, $CH_3CONHCSNHC_6H_5$, melting at 139°, although some hydrogen sulphide was evolved, did not lead to the formation of a triazole derivative, at least not as the chief product. The material that separated, on crystallizing from alcohol, formed large, four-sided plates melting at 153° and having all the properties of *phenylthiourea*. In other words, the action of phenylhydrazine, in this case, removes the acetyl group.

NEW HAVEN, May 29, 1900.

* Ber. d. chem. Ges., xxxii, 3658.

ON THE BEHAVIOR OF ACYLTHIONCARBAMIC ESTERS WITH ALKYL IODIDES AND AMINES: BENZOYLIMIDOTHIOCARBONIC ESTERS, ACYCLIC BENZOYLPSEUDOUREAS AND BENZOYLUREAS.

By HENRY L. WHEELER and TREAT B. JOHNSON.

In this paper we describe the results of an examination of some acetyl and benzoyl thioncarbamic esters as regards their behavior with alkyl iodides and with organic bases. This examination led us to the investigation of a series of benzoylimidothiocarbonic esters, $C_6H_5CO{-}N{=}C<{SR \atop OR'}$, acylpseudourea ethers, $C_6H_5CO{-}N{=}C<{NRR' \atop OR}$, and benzoylureas, $C_6H_5CONHCONRR'$, a preliminary account of which is also given.

The acylthioncarbamic esters are prepared by the union of acyl rhodanides with alcohols:

$$RCO{-}NCS + HOCH_3 = RCO{-}NHCS.OCH_3.\dagger$$

We find that these compounds have little tendency to undergo molecular rearrangement with alkyl iodides, a fact which is probably due to the negative character of the molecules. We observe that a rearrangement took place only in the case of the acetyl and benzoyl methyl esters when warmed, within narrow limits, with methyl iodide:

$$\underset{\text{I.}}{CH_3CO{-}NHCS.OCH_3} \rightarrow \underset{\text{II.}}{CH_3CONHCO.SCH_3}.$$

The same thiol compound (II) was obtained by warming methyl thiolcarbamate, $H_2NCO.SCH_3$, with acetic anhydride

* Amer. Chem. Jour., xxiv, No. 3.

† Miquel, Ann. Chim. Phys., 1877 [5], xi, 318.

on the water-bath, in the same way that Andreocci * found that xanthogenamide may be acetylated, this being the best method for the preparation of the acetylthioncarbamic esters.

These results show that the compounds formed by the union of acyl rhodanides with alcohols have the thion structure (I) which was assigned to them by Miquel † and Dixon,‡ and not the thiol structure as represented, subject to interrogation, in Beilstein's "Handbuch." §

We find that methyl benzoylthioncarbamate reacts more readily with chloracetic acid than with alkyl iodides, giving benzoylcarbaminthioglycollic acid:

$$C_6H_5CONHCS.OCH_3 \rightarrow C_6H_5CONHCO.SCH_2CO_2H.$$

In previous papers it has been shown that such thioncarbamic esters as have a more or less positive nature, ‖ especially the phenylthioncarbazinic esters,

$$C_6H_5NH{-}NHCS.OC_2H_5,\text{¶}$$

readily react with alkyl halides and with compounds of a negative character; while, on the other hand, with organic bases they proved to be quite inert.

We now find in the case of the negative benzoylthioncarbamic esters, $C_6H_5CO.NHCS.OR$, that the behavior is precisely the reverse. These compounds react with ammonia and organic bases at ordinary temperatures, but the course of the reaction is not what might, perhaps, be expected, since a smooth direct replacement, as represented by the following equation, does not take place:

$$C_6H_5CONHCS.\boxed{OCH_3 \quad H}NRR' = C_6H_5CONHCSNRR' + CH_3OH.$$

We find, instead of this, that the benzoylthioncarbamic esters unite with one molecule of a primary or secondary organic base,

* Ber. d. chem. Ges., xxv, R. 640.

† Loc. cit.

‡ J. Chem. Soc. (London), 1899, ccclxxviii.

§ Dritte Auflage, II, p. 1181.

‖ Wheeler and Barnes, Amer. Chem. Jour., xxii, 141.

¶ Ibid.

giving addition-products, which, we believe, are best represented by the general formula A.

$$\text{A.}\qquad C_6H_5CO{-}NHCS.OCH_3 + HNRR' = C_6H_5CO{-}\overset{H}{N}{-}C{\begin{array}{l}\diagup SH\\ -NRR'.\\ \diagdown OCH_3\end{array}}$$

The crude addition-products in most cases appear to be oils or varnishes which decompose more or less readily. We have isolated two examples of these, however, and in one case the product is a solid. An addition-product, as represented here, might be expected to decompose, on warming or on standing, in at least seven different ways, giving the following compounds or their decomposition-products:

$$\text{A.}\quad C_6H_5CO{-}\overset{H}{N}{-}C{\begin{array}{l}\diagup SH\\ -NRR'\\ \diagdown OCH_3\end{array}}\left\{\begin{array}{lr}\rightarrow C_6H_5CON{=}C{<}{\begin{array}{l}NRR'\\ OCH_3\end{array}} + H_2S & (1)\\ \rightarrow C_6H_5CONHCONRR' + CH_3SH & (2)\\ \rightarrow C_6H_5CONHCSNRR' + CH_3OH & (3)\\ \rightarrow C_6H_5CONRR' + H_2NCS.OCH_3 & (4)\\ \rightarrow C_6H_5CONH_2 + CH_3OCSNRR' & (5)\\ \rightarrow C_6H_5CONHCS.OCH_3 + HNRR' & (6)\\ \rightarrow C_6H_5CO.OCH_3 + H_2NCSNRR' & (7)\end{array}\right.$$

As a matter of fact, we have obtained examples of the first six of these modes of decomposition. The ease and manner in which the addition-products decompose depend mostly on the character of the amine radicals R and R′, and it may be stated that the above decompositions probably do not all take place in a single experiment. Generally, only two or three of them occur simultaneously. The most widely observed are represented by reactions (1) and (2), while of 13 amines which were allowed to act on benzoylmethyl and ethylthioncarbamic esters, reaction (3) was found to take place in quantity in only one instance.

For example, alcoholic ammonia reacts with ethyl benzoylthioncarbamate almost quantitatively according to (1). The aryl amines, aniline, toluidine, xylidine, *a*-naphthylamine, etc.,

and also benzylamine, react mostly according to (1) and to a less extent as represented by (2). A considerable evolution of hydrogen sulphide takes place (1), while mercaptan (2) is also noticed, and the corresponding benzoyl arylureas are easily isolated in a state of purity. The presence of benzoylpseudourea ethers (1) was established as shown below.

Diisobutylamine reacts with methyl benzoylthioncarbamate according to (1), (2), (3), and (4). On heating a mixture of these substances, which in the cold forms a varnish, hydrogen sulphide, mercaptan, and alcohol were evolved. The presence of benzoylpseudomethyldiisobutylurea, $C_6H_5CO—N{=}C{<}^{N(C_4H_9)_2}_{OCH_3}$, was established, and benzoyldiisobutylthiourea and diisobutylbenzamide were isolated.

Ethyl acetylthioncarbamate reacts with aniline, on warming, mostly according to (4), and β-naphthylamine was observed to behave in a similar manner with the benzoylmethyl ester.

Diisoamylamine unites with methyl benzoylthioncarbamate giving an example of the addition-product A, which is a solid at ordinary temperatures. The ester and amine combine when mixed in molecular proportions, with evolution of heat, but no gas is given off until the addition-product is heated to about 80°, the decomposition then proceeding chiefly according to (5) and (1). Hydrogen sulphide is evolved and benzamide (5) and diamylamine are obtained as the chief products of the reaction. The same products are obtained when hydrogen sulphide is passed into benzoylpseudomethyldiisoamylurea, $C_6H_5CO—N{=}C{<}^{N(C_5H_{11})_2}_{OCH_3}$, at 60°. The fact that the pseudourea ether is not obtained here, at least not as the chief product, is therefore explained. The presence of diisoamylthiourethane was looked for, but it was not found. When this addition-product is allowed to stand over sulphuric acid, a slow decomposition or dissociation according to (6) takes place.

The addition-product in the case of diethylamine differs from the above, inasmuch as it is an oil which, on standing, gives benzamide.

Although in every case more or less hydrogen sulphide was evolved in the action of amines on the acylthioncarbamic esters, thus indicating the formation of acylpseudourea ethers, nevertheless these interesting compounds could not be isolated from the other by-products in these reactions (except in the case of ammonia). They form oils which cannot be distilled out of the mixture, without decomposition, even under reduced pressure. Their presence was established, however, not only by the fact that hydrogen sulphide was evolved, but also by the comparison of the properties of the reaction-products with those of the corresponding acylpseudourea ethers. We prepared the latter from the benzoylimidothiocarbonic esters, $C_6H_5CO—N{=}C{<}^{SR}_{OR}$, and it was found that the action of dilute hydrochloric acid affords a delicate test for their presence (see below).

The benzoylimidothiocarbonic esters are readily formed by the action of alkyl iodides on the sodium or potassium salts of the benzoylthioncarbamic esters* in the same manner as it has been found in general that the derivatives of the thioncarbamic esters react in the pseudoform, giving the substituted imidothiocarbonic esters: †

$$C_6H_5CONHCS.OC_2H_5 \rightarrow \overset{\text{III.}}{C_6H_5CO—N{=}C{<}^{SC_2H_5}_{OC_2H_5}}.$$

Hitherto, only one compound of this series has been isolated. Lössner obtained diethyl benzoylimidothiocarbonate (III) in the above manner. He states that it is an oil which decomposes at 44°, giving off mercaptan; while at higher temperatures benzonitrile and a syrupy residue are obtained. He assigned the incorrect formula, $C_6H_5CON(C_2H_5)CO.SC_2H_5$, to this substance, and the solid obtained by treating this with

* Lössner, J. prakt. Chem., 1874 [2], x, 237; Dixon, J. Chem. Soc. (London), 1899, 380.

† Liebermann, Ann. Chem. (Liebig), cclxx; Busch and Lingenbrink, Ber. d. chem. Ges., xxxii, 2620; Fromm and Block, Ibid., 2212; and Wheeler and Barnes, Amer. Chem. Jour., xxiv, 60.

ammonia was regarded as benzoylethylurea. Dixon,* however, has shown that this is really a pseudourea.

The benzoylimidothiocarbonic esters, when prepared as described below, are oils without exception, which, as far as we have observed, distil unaltered under reduced pressure. For example, the oil of Lössner, when pure, has an odor like the xanthic esters, and it boils at about 210° at 19 mm. pressure, without the slightest sign of decomposition. The reaction which affords these oils is so smooth that for most purposes it is unnecessary to distil them. In some of our experiments the ether solutions of the crude products, after washing, were thoroughly dried over calcium chloride and then evaporated in a vacuum at 100°. Under these conditions the only impurity that appears to be present is benzamide, and then, if heating has been avoided before drying, only in very small quantities. When the oils are heated with water, they give benzamide: †

IV.

$$C_6H_5CON{=}C{<}^{SC_2H_5}_{OC_2H_5} \rightarrow$$
$$C_6H_5CONH_2 + CO_2 + C_2H_5OH + C_2H_5SH.$$

We find that with hydrogen sulphide at 100° the following takes place:

V.

$$C_6H_5CO{-}N{=}C{<}^{SCH_3}_{OCH_3} \rightarrow C_6H_5CO\overset{H}{N}{-}C{\begin{smallmatrix}\diagup SCH_3\\ -SH\\ \diagdown OCH_3\end{smallmatrix}} \rightarrow$$
$$C_6H_5CO\overset{H}{N}{-}CS.OCH_3.$$

The ester is converted into benzoylthioncarbamic ester with loss of mercaptan.

That the oils obtained in the above manner are homogeneous is shown in each case by their smooth reactions with hydrogen chloride and with organic bases. We have obtained instances of the two following decompositions when the oils are dissolved in benzene and treated at ordinary temperatures with dry hydrogen chloride:

* Loc. cit. † Lössner, loc. cit.

VI.

$$C_6H_5CO{-}N{=}C{<}{}^{SC_2H_5}_{OCH_3} \rightarrow C_6H_5CO{-}\overset{H}{N}{-}C{\begin{smallmatrix} \diagup SC_2H_5 \\ -\,\boxed{Cl} \\ \diagdown O\boxed{CH_3} \end{smallmatrix}}$$

VII.

$$C_6H_5CO{-}N{=}C{<}{}^{SC_5H_{11}}_{OCH_3} \rightarrow C_6H_5CO{-}\overset{H}{N}{-}C{\begin{smallmatrix} \diagup S\boxed{C_5H_{11}} \\ -\,\boxed{Cl} \\ \diagdown OCH_3 \end{smallmatrix}}$$

The decomposition with hydrogen chloride proceeds, with the series $C_6H_5CO{-}N{=}C{<}{}^{SAlk}_{OCH_3}$, chiefly or entirely according to reaction VI, giving benzoylthiolcarbamic esters. When the alkyl group is amyl, it separates according to reaction VII.

When the benzoylimidothiocarbonic esters are treated with organic bases, they readily react, giving off mercaptan and forming acylpseudourea ethers. The reaction is, in all probability, perfectly analogous to that of the above-mentioned benzoylthioncarbamic esters, except that the intermediate addition-product B (below) decomposes more smoothly and not in such a variety of ways as found in the case of the addition-product A. In most cases the reaction appears to take place quantitatively, as follows:

B.

$$C_6H_5CO{-}N{=}C{<}{}^{SR}_{OCH_3} + HNR'R'' \rightarrow C_6H_5CO{-}\overset{H}{N}{-}C{\begin{smallmatrix} \diagup SR \\ -\,NR'R'' \\ \diagdown OCH_3 \end{smallmatrix}} \rightarrow$$

$$C_6H_5CO{-}N{=}C{<}{}^{NR'R''}_{OCH_3} + HSR.$$

It appears that previously this action has only been investigated with ammonia, Dixon having shown that methyl- and ethyl-ψ-n-benzoylureas are formed in this way. He obtained these acylpseudourea ethers as crystalline compounds melting at 74°–75° and 77°–78°, respectively.

The compounds of this type which we have obtained with organic bases are oils. Those which we attempted to distil

decomposed. They appear to be even more reactive than the interesting series of pseudourea ethers first obtained by Lengfeld and Stieglitz,* which have been so thoroughly studied by Stieglitz and Dains.† In properties they are closely similar to the acylimido-esters ‡ and acylamidines, § to both of which series the compounds belong, since they have the structure of both these classes combined. We find that the most striking reaction, at present, of this series of benzoylpseudourea ethers is the ease with which they act with hydrochloric acid. Most of the pseudourea ethers mentioned above, as well as those described by Stieglitz and McKee,‖ give salts with hydrochloric acid from which platinum double salts can be prepared. In stability, they approach the salts of the imido-ethers prepared by Pinner and others. We observed similar properties among the benzoylpseudourea ethers in the case of those prepared with ammonia. For example, benzoylpseudoethylurea, $C_6H_5CO—N=C<{NH \atop OC_2H_5}$, dissolves in cold hydrochloric acid, and gold chloride gives a bright-yellow precipitate of fine needles. A gold determination in this agreed with the formula $C_6H_5CO—N=C<{NH_2 \atop OC_2H_5}.HCl.AuCl_3$. This salt is quite stable, and it melts with decomposition at about 140°.

When, on the other hand, the more negative benzoylpseudourea ethers, especially those containing aryl groups, are treated with cold, aqueous hydrochloric acid, a reaction starts immediately. The solutions effervesce, alkyl chloride being driven off, whereupon, as a rule, the oils are quantitatively converted into beautifully crystallizable colorless acylureas. In the case of the aryl derivatives, the oils crystallize immediately, while the alphyl compounds solidify more slowly.

* Ber. d. chem. Ges. (1894), xxvii, 926.

† Jour. Amer. Chem. Soc., xxi, 136.

‡ Wheeler and Walden, Amer. Chem. Jour., xix, 129; Wheeler, Walden, and Metcalf, Ibid., xx, 64; and xix, 217.

§ Wheeler and Walden, Ibid., xx, 569.

‖ Ber. d. chem. Ges., xxxiii, 807.

This is in striking contrast to some of the pseudourea ethers of Stieglitz and Dains, which are not completely decomposed by cold aqueous hydrochloric acid after a month's standing.

The following represents the course of the reaction with hydrochloric acid:

IX.

$$C_6H_5CO{-}N{=}C\begin{matrix}\diagup NRR' \\ \diagdown OCH_3\end{matrix} \rightarrow C_6H_5C\overset{H}{O}N{-}C\begin{matrix}\diagup NRR' \\ -Cl \\ \diagdown O\,CH_3\end{matrix} \rightarrow$$

$$\begin{matrix} C_6H_5CONHCONRR' \\ + \\ CH_3Cl \end{matrix}$$

This sensitiveness to hydrochloric acid finds a perfect parallel in the deportment of the acylimido-esters, and it is shared also to a less extent by the acylamidines. The results show that the more negative the character of the radical in the imido-ester grouping, $RN{=}CR'.OR''$, the more sensitive are the compounds in regard to decomposition by hydrogen chloride, a fact also noticed by Stieglitz and Dains in other cases.

In this connection it is interesting to note that pure water has little tendency to react with most of the benzoylpseudourea ethers. This is well illustrated by the fact that Dixon, in showing the structure of the acylpseudourea ether,

$$C_6H_5CON{=}C{<}\begin{matrix}NH_2 \\ OCH_3\end{matrix},$$

heated the compound in closed tubes with ten parts water from 105° to 125° "without any sign of change. On raising the temperature to 150 –168° action occurred, carbonic anhydride escaped on opening the tube, the liquid contents of which smelt of ammonia and methyl benzoate." In other words, the material refused to react with water without total decomposition.

On the other hand, we find that if this compound, which melts at 77°, is gently warmed with water, in the presence of hydrochloric acid, it fuses, but in a few moments it solidifies,

whereupon the material is quantitatively converted into benzoylurea, $C_6H_5CONHCONH_2$, melting at 214°. The above procedure affords a smooth method for the preparation of most of the *α-β*-benzoylureas, since the different steps of the process give almost quantitative yields.

We hope later to describe other reactions of the acylpseudourea ethers.

The acylthioncarbamic esters react with phenylhydrazine, giving off hydrogen sulphide in the cold. The products, however, are not pseudourea or pseudosemicarbazidic esters, as might be expected, but the following ring-formed compounds:

X.

That the products are alkyloxytriazoles is shown by the behavior of the compound from methyl benzoylthioncarbamate. This, when boiled with hydrochloric acid, slowly gives up the methyl group, and the so-called 1,5-diphenyl-3-oxytriazole (1,5-diphenyl-3-triazolone?) is obtained:

XI.

The product (XI) is identical with that obtained by Young * from phenylsemicarbazide and benzaldehyde, and by Widman † from benzoylsemicarbazide by treating with alkali.

Phenylhydrazine, therefore, reacts with the thionacylurethanes in a different manner than with the ordinary acylurethanes, inasmuch as Andreocci ‡ found that acetylurethane gives 1-phenyl-3-methyl-5-triazolone, while the above reactions lead to the formation of the isomeric compound, 1-phenyl-5-methyl-3-triazolone.

* Ber. d. chem. Ges., xxix, 2311.

† Ibid., xxix, 1951.

‡ Ibid., xxii, R. 737.

EXPERIMENTAL PART.

The Action of Acylthioncarbamic Esters with Organic Halides.

Preparation of Methyl Acetylthioncarbamate, $CH_3CO—NHCS.OCH_3$. — In our first experiments we boiled acetyl chloride in benzene solution with an excess of lead sulphocyanide for several hours; methyl alcohol was then added, in slight excess, and the mixture boiled for about thirty minutes. On evaporating, an oil was obtained, which, on cooling, solidified. It was crystallized from petroleum ether, when it separated in arborescent crystals melting at 79°–80°. It is readily soluble in water, alcohol, benzene, and chloroform, and when boiled with freshly precipitated mercuric oxide, it is desulphurized. A nitrogen determination gave:

	Calculated for $C_4H_7NO_2S$.	Found.
N	10.52	10.12

This compound is more easily obtained by warming methyl thioncarbamate with acetic anhydride on the water-bath. We found later that it is unnecessary to use lead sulphocyanide for the preparation of either acetyl or benzoyl rhodanide. In order to obtain a good yield of acetyl rhodanide, acetyl chloride is boiled with an excess of finely pulverized potassium sulphocyanide, in the presence of a little toluene, and under a pressure of about 900 mm. of mercury. In the case of benzoyl rhodanide, an increase in pressure is unnecessary, for example: 15 g. of benzoyl chloride were boiled with 10.5 g. of potassium sulphocyanide in 10 c. c. of toluene for fifteen minutes, and then the material was distilled at 36–35 mm. pressure, when, below 90°, the toluene was collected; from 142° to 151° only a few drops distilled over; and then from 151° to 151.5° the entire remainder was obtained except an insignificant colored residue. The last fraction consisted of practically pure rhodanide.

Methyl Acetylthiolcarbamate, $CH_3CO—NHCO.SCH_3$.— We observed the formation of this compound when 4 g. of methyl acetylthioncarbamate were allowed to stand with one molecular proportion of methyl iodide, in a sealed tube at 40°–45°, for three weeks. The material, when crystallized from benzene, separated in the form of fine needles, melting at 145.5°–146°. It is insoluble in cold water, but readily soluble in hot water and in alcohol. It was not desulphurized when boiled with mercuric oxide, and a nitrogen determination gave:

	Calculated for $C_4H_7NO_2S$.	Found.
N	10.52	10.15

When methyl acetylthioncarbamate was heated with an excess of methyl iodide on the steam-bath for from six to seven hours, no molecular rearrangement occurred, and no change was noticed when the mixture was allowed to stand at ordinary temperature for three weeks. That a rearrangement had taken place in the first experiment was shown by the fact that the compound melting at 145.5°–146° can also be prepared by warming methyl thiolcarbamate with acetic anhydride on the water-bath.

Ethyl Acetylthioncarbamate, $CH_3CO—NHCS.OC_2H_5$, was prepared like the methyl ester. Dixon * has shown that when pure acetyl rhodanide is mixed with alcohol a violent reaction takes place, fused sulphur and other products being obtained. However, this ester can be prepared from the rhodanide if the latter is mixed with benzene. It is difficultly soluble in water, but readily soluble in alcohol and benzene. From water it crystallizes in prisms and melts at 100°–101°. A nitrogen determination gave:

	Calculated for $C_5H_9NO_2S$.	Found.
N	9.5	9.9

Attempts to arrange this thion ester into the isomeric thiol compound were without success. When heated with ethyl

* Jour. Chem. Soc. (London), lxi, 529.

iodide in a closed tube to 100°, ammonium iodide was obtained as the only solid product. When heated from 80° to 90°, a product was obtained crystallizing in plates and melting at 105°–106°, and otherwise having all the properties of ethyl thiolcarbamate, $H_2NCO.SC_2H_5$. When allowed to stand dissolved in ethyl iodide for four months, no action was observed. This is in marked contrast with the ease with which xanthogenamide and ethyl thionphenylcarbazinate undergo a molecular rearrangement.

Methyl Benzoylthioncarbamate, $C_6H_5CO—NHCS.OCH_3$.— This and the following ethyl ester were prepared by boiling benzoyl chloride, diluted with a little toluene, with an excess of potassium sulphocyanide. For 100 g. of benzoyl chloride the reaction was practically complete in a few hours; then, on cooling, alcohol was added and warmed for a short time. The toluene was then removed in a current of steam and the residue crystallized from dilute alcohol, when the ester separated in needles melting at 97°, as stated by Miquel.*

Methyl Benzoylthiolcarbamate, $C_6H_5CO—NHCO.SCH_3$.— This compound was obtained when 8 g. of the above ester were heated with methyl iodide in a closed tube from 80° to 90° for six hours. On opening the tube it was found to be filled with a mass of beautiful, long prisms, some of them from 1 to 2 inches in length. On crystallizing these from alcohol they melted at 152°–153°, and a nitrogen determination gave:

	Calculated for $C_9H_9NO_2S$.	Found.
N	7.1	6.9

This thiol ester is soluble in alkali and is precipitated unaltered by acids. When boiled with mercuric oxide, it gave no precipitate of mercuric sulphide, thus differing from the thion ester.

When the thion ester was heated with methyl iodide to 100°–110°, decomposition took place, and a compound free from sulphur and difficultly soluble in alcohol was obtained. It was insoluble in hot water and sodium hydroxide, and it sepa-

* Loc. cit.

rated from alcohol in small needles, melting at about 215° with effervescence. It crystallizes unaltered from nitric acid, and a nitrogen determination gave 11.1 per cent. It was not identified.

Ethyl Benzoylthioncarbamate, $C_6H_5CO—NHCS.OC_2H_5$.—This compound was first obtained by Lössner,* the structure $\genfrac{}{}{0pt}{}{C_6H_5CO}{C_2H_5}\!>\!NCO.SH$ being assigned to it, while in Beilstein's "Handbuch" it is represented by the formula

$$C_6H_5CONHCO.SC_2H_5\ (?)$$

Its correct formula, the thion structure, was given to it by Miquel * and further confirmed by Dixon.* For our use we prepared it from the rhodanide as above stated. It forms colorless needles from dilute alcohol and it melts at 73°–74°. It is desulphurized by boiling with mercuric oxide, and it has little if any tendency to undergo a molecular rearrangement with ethyl iodide. It was not changed by standing for two weeks with ethyl iodide or by heating it from 95° to 100° or from 100° to 110°. When heated with the iodide from 125° to 130° for four hours, benzamide was obtained.

Benzoylcarbaminthioglycollic Acid, $C_6H_5CONHCO.SCH_2COOH$.—When molecular quantities of methyl benzoylthioncarbamate and chloracetic acid were heated for eight hours on the steam-bath, a slow effervescence took place. The product, then crystallized from dilute alcohol, gave colorless needles melting at 169°–170°. This material was not desulphurized by boiling with mercuric oxide. It is soluble with difficulty in benzene, and a nitrogen determination gave:

	Calculated for $C_{10}H_9NO_4S$.	Found.
N	5.8	6.1

Benzoylurea, $C_6H_5CO—NHCONH_2$.—On treating the above compound, dissolved in alcohol, with ammonia, a mass of small lozenge-shaped plates separated. This material was free from sulphur and melted from 214° to 215° with slight

* Loc. cit.

effervescence. It was soluble in hot water and in sodium hydrate, and was precipitated from the latter solution unaltered by hydrochloric acid. A nitrogen determination gave:

	Calculated for $C_8H_8N_2O_2$.	Found.
N	17.0	16.7

It was stated by Zinin,* who first obtained benzoylurea, that this compound melts "gegen 200°." Geuther, Scheitz, and Marsh † give 208°. That these melting-points are too low is shown by the above; moreover, we have obtained benzoylurea by other methods, and in each case it was found to melt at 214°–215°.

Methyl Dibenzoylthioncarbamate, $(C_6H_5CO)_2NCS.OCH_3$.— The sodium salt of methyl benzoylthioncarbamate was prepared by dissolving the ester in methyl alcohol, adding a strong solution of sodium methylate, and then precipitating with ether. Thus prepared, it formed a sandy powder which was dried over sulphuric acid in a vacuum. On treating this, suspended in benzene, with the calculated quantity of benzoic anhydride, and boiling for six hours, an oil was obtained which solidified on cooling. On crystallizing this from petroleum ether, colorless plates separated which melted, when pure, at 81°–82°, and a nitrogen determination gave the following result:

	Calculated for $C_{16}H_{13}NO_3S$.	Found.
N	4.6	4.7

When this diacylthiourethane was treated with a molecular proportion of phenylhydrazine in the cold, hydrogen sulphide was evolved, and, on crystallizing the product from benzene, needles or prisms were obtained melting at 166°–167°, which proved to be benzoylphenylhydrazine.

When the sodium salt of methyl benzoylthioncarbamate was treated in dry benzene with acetic anhydride, and the product crystallized from dilute alcohol, nothing but unaltered ester was obtained.

* Ann. Chem. (Liebig), xcii, 404. † Zeitschr. Chem., 1868, 305.

Methylene Thiolcarbamate, $H_2NCO.SCH_2S.CONH_2$. — Gabriel and Heyman [*] found that ethylene bromide and thioamides give thiazoline derivatives, while Pinkus [†] obtained from trimethylene chlorobromide and thioamides the so-called penthiazolines. In the case of xanthogenamide, he found that the reaction gave a compound or mixture agreeing with the formula, $C_4H_8NOS\frac{Br + Cl}{2}$. Recently Busch [‡] has found that the potassium salts of the dithiocarbazinic esters give ring-formed compounds with ethylene bromide, diazthins, and not the ethylene esters. In a recent paper Wheeler and Barnes [§] have described the action of ethylene bromide on xanthogenamide. They obtained a product which appeared to be the ethylene ester of thiolcarbamic acid. It therefore seemed of interest to determine whether other alkyl dihalides also act abnormally with xanthogenamide. For this purpose we warmed methylene iodide with xanthogenamide in molecular proportions for five hours on the steam-bath, when the odor of the iodide disappeared. On cooling and crystallizing from water, small compact crystals were obtained, melting at 168°–170°, which, on analysis, gave the following result:

	Calculated for $C_3H_6O_2N_2S_2$.	Found.
N	16.8	16.3

Ethylene Thiolcarbamate, $H_2NCO.SCH_2{-}CH_2S.CONH_2$, from ethylene bromide and xanthogenamide, has already been described, [||] but the melting-point was omitted; it melts at 231°–232°.

Trimethylene Thiolcarbamate, $H_2NCO.SCH_2CH_2CH_2S.CONH_2$, from trimethylene bromide and xanthogenamide, after two hours' heating on the water-bath, crystallizes from hot water in plates, and melts at 177°–179°. It is extremely soluble in alcohol and difficultly soluble in benzene. A nitrogen determination gave:

* Ber. d. chem. Ges., xxiii, 157; xxiv, 783.
† Ibid., xxvi, 1083.
‡ J. prakt. Chem., lx, 26.
§ Amer. Chem. Jour., xxii, 151.
|| Wheeler and Barnes, loc. cit.

	Calculated for. $C_6H_{10}O_2N_2S_2$.	Found.
N	14.4	14.1

When *isobutylene bromide* and xanthogenamide were heated on the water-bath for five hours, cyanuric acid, ethyl thiolcarbamate, and unaltered material were obtained.

The Behavior of Acylthioncarbamic Esters with Ammonia and Amines.

Ethyl Benzoylthioncarbamate and Ammonia. — 5 g. of the ester were dissolved in an excess of alcoholic ammonia and the solution allowed to stand at rest for three days. The action began immediately, and hydrogen sulphide was slowly evolved at ordinary temperatures. After the action was complete the alcohol was distilled off, and the first portions were tested for mercaptan, but with a negative result. When most of the alcohol had evaporated, the remaining solution was poured into dilute potassium hydrate, when an oil separated which soon solidified. On crystallizing this from petroleum ether, beautiful, long, needle-like prisms separated, which melted sharply at 74°–75°. This compound has practically the same melting-point as ethyl benzoylthioncarbamate; but that it was not this substance was shown by mixing the two, when the mixture melted at 45°. The properties of the substance show that it is identical with the compound first obtained by Lössner, which Dixon has shown has the formula,

$$C_6H_5CO{-}N{=}C{<}^{NH_2}_{OC_2H_5}.\ *$$

In other words, it is *benzoylpseudoethylurea.* The reaction appears to be practically quantitative. When this substance is treated with dilute hydrochloric acid, it dissolves, and on gently warming the solution and again cooling, *benzoylurea,* melting at 214°–215°, separates.

Benzoylpseudoethylurea Chloraurate, $C_6H_5CO{-}N{=}C(NH_2).OC_2H_5.HCl.AuCl_3$, is precipitated from the above hydrochloric acid solution on the addition of gold chloride. It forms fine,

* Loc. cit.

bright-yellow needles, which are difficultly soluble in water and melt at about 140°. A gold determination gave:

	Calculated for $C_{10}H_{13}N_2O_2Cl_4Au$.	Found.
Au	37.0	37.1

Methyl Benzoylthioncarbamate and Diethylamine unite at ordinary temperature, without evolution of gas, to form a varnish which refused to solidify on cooling or on keeping in a vacuum desiccator over sulphuric acid for two to three days. At the end of this time free amine appeared to be absent, and a nitrogen determination gave 9.89 per cent nitrogen instead of 10.49, which is required for

$$C_6H_5CONHCS.OCH_3.HN(C_2H_5)_2.$$

The result is, perhaps, as close as could be expected, considering the fact that the material does not permit of a better method of purification. The material, on standing for three weeks in a desiccator, deposited benzamide. On heating, the result was the same; hydrogen sulphide and other products were given off, and only a small amount of oil besides benzamide was obtained. It dissolves very readily in alcohol and benzene, and is precipitated as an oil by petroleum ether.

Ethyl Benzoylthioncarbamate and Diisobutylamine combine to form a varnish as in the previous case. When 16 g. of the ether were heated with 10 g. of the amine, reaction began at about 80°, and 600 c. c. of hydrogen sulphide were collected over water, and the presence of alcohol and mercaptan was also identified in the volatile products. On cooling, a thick oil was obtained which, when treated with hydrochloric acid, gave off ethyl chloride and solidified completely. On crystallizing then from strong alcohol, colorless prisms separated which occurred in twins, in the form of beautiful crosses, and melted at 130°–132°. This material was found to contain sulphur, and a nitrogen determination agreed with the calculated for *benzoyldiisobutylthiourea*, $C_6H_5CONHCSN(C_4H_9)_2$.

	Calculated for $C_{16}H_{24}N_2OS$.	Found.
N	9.59	9.95

A portion of the above product, which had not been treated with hydrochloric acid, was distilled at 25 mm. pressure, when, after decomposition of some constituent (the pseudo-urea ether (?)), a considerable portion of oil distilled over between 182° and 190°. This was redistilled at ordinary pressure, when it boiled mostly from 288° to 311°; it was then treated with alkali, and the insoluble part was extracted with ether, whereupon, on evaporating, a brilliant mass of stout prisms separated. This compound was purified by crystallizing from petroleum ether. It melted at 65°, and a nitrogen determination agreed with the calculated for *diisobutylbenzamide*:

$$C_6H_5CO—N(C_4H_9)_2.$$

	Calculated for $C_{15}H_{23}NO$.	Found.
N	6.0	6.4

The alkaline solution, on acidifying, gave benzoyldiisobutylthiourea. Diisobutylbenzamide, like its homologues, is very soluble in most organic solvents, from which solutions it is obtained as an oil which solidifies to form beautiful crystals.

Methyl Benzoylthioncarbamate and Diisoamylamine combine with a decided evolution of heat, to form an oil which quickly solidifies. No trace of mercaptan or hydrogen sulphide is given off at ordinary temperatures and, when this addition-product is prepared by mixing molecular quantities, it melts at 55°–60°. It is extremely soluble in benzene and alcohol, and apparently undergoes dissociation, since petroleum ether precipitates unaltered methyl benzoylthioncarbamate. On standing in a desiccator over sulphuric acid, it slowly decomposed, becoming oily (separation of free amine), when after a week unaltered ester was obtained. As it could not be purified by crystallization, a portion was prepared by mixing 5 g. of the ester with about 4 g. of diamylamine and grinding the material together in a mortar, after which it was thoroughly pressed on paper and allowed to stand exposed to the air for a short time. A nitrogen determination then gave 8.6 per cent of nitrogen, while the calculated for

$C_6H_5CONHCSOCH_3.HN(C_5H_{11})_2$

is 7.9 per cent; the calculated for unaltered ester being 7.1 per cent.

When the addition-product was heated, evolution of hydrogen sulphide and mercaptan was noticed at its melting-point, and, on maintaining the temperature at about 80°, an oil was obtained which, when treated with benzene, deposited plates. These were crystallized from water, whereupon they melted from 126° to 127°; they were free from sulphur, and a nitrogen determination gave results agreeing with the calculated for *benzamide*.

	Calculated for C_7H_7NO.	Found.
N	11.5	11.2

An attempt was made to isolate the pseudourea ether that is formed here, which constitutes the oil removed by benzene in the above experiment. With this aim we tried distilling the addition-product at 15 mm. pressure; on heating, the pressure rose to 40 mm., and up to 200° an oil and a solid distilled over. The oil consisted mostly of benzonitrile and the solid was benzamide. When this pseudourea ether is treated with cold hydrochloric acid, methyl chloride is evolved and benzamide and diamylamine hydrochloride are obtained. The formation of benzoyldiisoamylurea was not observed.

Ethyl Benzoylthioncarbamate and Benzylamine energetically react with evolution of heat; hydrogen sulphide and mercaptan are apparently evolved, and the mixture readily solidifies. On crystallizing then from 95 per cent alcohol, flattened prisms separate which melt sharply at 89°. The material does not contain sulphur, and a nitrogen determination agrees with the calculated for *benzoylbenzylurea*, $C_6H_5CONHCONHCH_2C_6H_5$.

	Calculated for $C_{15}H_{14}N_2O$	Found.
N	11.0	10.7

Ethyl Benzoylthioncarbamate and Aniline. — 10 g. of the former were mixed with one molecular proportion of the latter

and the mixture was warmed for from eight to nine hours on the steam-bath, when hydrogen sulphide ceased being evolved and an oil was obtained. On standing, crystals separated which formed an arborescent mass from dilute alcohol, and melted at 202°–203°. This material was free from sulphur, and a nitrogen determination gave the following result:

	Calculated for $C_{14}H_{12}N_2O_2$.	Found.
N	11.66	11.68

This material agrees in properties with *benzoylphenylurea*, $C_6H_5CONHCONHC_6H_5$, which Blacher * has prepared by another method. He gives its melting-point as 204°–205°. This compound has also been obtained by Kuhn,† who states that it melts at 199°, and also by Beckmann and Köster, who give 204° as its melting-point.

Ethyl Benzoylthioncarbamate and Paratoluidine. — A mixture of these substances in molecular proportions was heated for from seven to eight hours on the steam-bath. Hydrogen sulphide was given off during the reaction; the product thus obtained consisted chiefly of pseudoethylparatolylbenzoylurea, $C_6H_5CON{=}C(OC_2H_5){-}NHC_6H_4CH_3$, and was an oil which on exposure to the laboratory atmosphere deposited crystals after two days. On pressing these on a plate and crystallizing from dilute alcohol, small narrow prisms were obtained which melted at 80°–81°. These were free from sulphur, and a nitrogen determination showed that this material was *benzoylparatolylurea*, $C_6H_5CO{-}NHCONHC_6H_4CH_3$.

	Calculated for $C_{15}H_{14}N_2O_2$.	Found.
N	11.0	10.7

In order to show the presence of pseudoethylparatolylurea, 3 g. of methyl benzoylcarbamate and 1.6 g. of toluidine were heated together; a lively effervescence of hydrogen sulphide took place at 90°, and in about one hour, with these quanti-

* Ber. d. chem. Ges., xxviii, 435.
† Ibid., xvii, 2881.
‡ Ann. Chem. (Liebig), cclxxiv, 28.

ties, it practically ceased. The oil thus obtained was treated with 10 c.c. of about 20 per cent hydrochloric acid, and the gas which was evolved was collected over water, in which it was partly soluble. In one hour over 80 c.c. of methyl chloride were obtained. When methyl benzoylthioncarbamate was treated with hydrochloric acid under the same conditions, no gas was evolved. On warming, however, methyl chloride is evolved.

With the object of isolating the pseudourea ether that is formed in this reaction, we subjected the reaction-product to distillation, starting at 13 mm. pressure. At 165° the pressure rose, and up to 200°, at 20 mm. pressure, a portion had distilled over; in this we identified benzamide and benzonitrile, which showed that the material had decomposed.

When ethyl acetylthioncarbamate was warmed with *p*-toluidine, hydrogen sulphide was evolved, and an oil and a solid were obtained; on crystallizing the solid from alcohol, it melted at 147° and had all the properties of paracettoluide. The oil was not examined.

Ethyl Benzoylthioncarbamate and 2,4-Dimethylaniline were heated together in molecular proportions on the water-bath, and an attempt was made to collect the mercaptan given off, but it was carried off in the stream of hydrogen sulphide which escaped. On cooling, an oil was obtained together with some solid. The solid was filtered off and, on crystallizing from alcohol, it melted at 215°–217°. On treating the oil with hydrochloric acid, ethyl chloride was evolved and the material solidified, when, on crystallizing from alcohol, it likewise melted at 215°–217°. A nitrogen determination gave:

	Calculated for $C_{16}H_{16}N_2O_2$.	Found.
N	10.4	10.5

This compound is therefore *a, β-benzoylmetaxylylurea*,

$$C_6H_5CONHCONHC_6H_3(CH_3)_2.$$

Ethyl Benzoylthioncarbamate and p-Anisidine reacted at once with a rapid evolution of hydrogen sulphide. When warmed

on the water-bath until this ceased, and then cooled, very little oil was obtained. The chief quantity of the reaction-product was solid. From this, two compounds were separated by means of alcohol and benzene. The more soluble one, the chief product, proved to be benzoylparaanisidine. Boiling the product with alcohol gave a mass of colorless prisms which melted at 216°–218°, and a nitrogen determination of this substance, which burns slowly, gave the following result:

	Calculated for $C_{15}H_{14}N_2O_3$.	Found.
N	10.3	9.8

This material is therefore *benzoylparamethoxyphenylurea*,

$$C_6H_5CONHCONHC_6H_4OCH_3.$$

When the above oil was treated with hydrochloric acid, it gave off ethyl chloride, showing the presence of benzoylpseudoethylparamethoxyphenylurea.

Methyl Benzoylthioncarbamate and α-Naphthylamine. — On warming molecular quantities of these substances until hydrogen sulphide ceased coming off, an oil was obtained which, treated with benzene and petroleum ether, gave a precipitate. When this was boiled with alcohol, a residue of cyanphenine, melting at 230°, remained. On adding water to the alcoholic solution, and then crystallizing from dilute alcohol, we obtained colorless prisms melting at 165°–166°. This material contained no sulphur. That it was not benzoyl-α-naphthalide, which melts at 160°–162°, was shown on mixing these substances, when the mixture melted at 140°. A nitrogen determination agreed with the calculated for *benzoyl-α-naphthylurea*,

$$C_6H_5CONHCONHC_{10}H_7.$$

	Calculated for $C_{18}H_{14}N_2O_2$.	Found.
N	9.6	9.8

Methyl Benzoylthioncarbamate and β-Naphthylamine gave off hydrogen sulphide on warming, thus showing the formation of a pseudourea ether. The product was obtained as an oil that deposited nothing solid on standing a week. On add-

ing petroleum ether and crystallizing from dilute alcohol, small needles separated which melted at 156°. The material contained no sulphur, and a nitrogen determination gave results agreeing with the calculated for *benzoyl-β-naphthamide.*

	Calculated for $C_6H_5CONHCONHC_{10}H_7$.	Calculated for $C_6H_5CONHC_{10}H_7$.	Found.
N	9.65	5.46	5.26

Ethyl Benzoylthioncarbamate and Diphenylamine react with difficulty, and hydrogen sulphide is given off. After heating for three days on the steam-bath an oil was obtained which, when treated with hydrochloric acid, decomposed with the separation of diphenylamine.

Ethyl Benzoylthioncarbamate and Orthophenylenediamine were mixed in the proportion of 2 molecules of the former to 1 of the latter in ether solution, when, on evaporating, hydrogen sulphide was given off and a solid was directly obtained. There appeared to be little or no oil in this case. The material, when crystallized from alcohol, separated in lozenge-shaped crystals, which were free from sulphur; they melted at 235°, and a nitrogen determination agreed with the calculated for *dibenzoylphenylen diurea,*

$$C_6H_5CONHCONHC_6H_4NHCONHCOC_6H_5.$$

	Calculated for $C_{22}H_{18}N_4O_4$.	Found.
N	13.9	14.2

Methyl Benzoylthioncarbamate and Phenylhydrazine.—When phenylhydrazine is added to the ester, the mixture becomes warm and hydrogen sulphide is given off. On heating, to complete the action, and then cooling, an oil is obtained which readily solidifies. On crystallizing this from dilute alcohol, colorless needles are obtained melting at 85°–86°. A nitrogen determination agreed with the calculated for *1,5-diphenyl-3-ethoxytriazole.* This material was free from sulphur.

	Calculated for $C_{15}H_{13}N_3O$.	Found.
N	16.7	16.9

1-5-Diphenyl-3-triazolone was obtained when the above was boiled with concentrated hydrochloric acid in alcoholic solution for from eight to nine hours.

Ethyl Acetylthioncarbamate and Phenylhydrazine reacted in the cold, giving off hydrogen sulphide, but on standing two weeks nothing solid separated. The material was then distilled at 17–18 mm. pressure, whereupon it practically all boiled from 190° to 193°. This readily solidified and, on crystallizing from petroleum ether, it formed long, stout prisms, melting at 49°–50°. It is extremely soluble in alcohol and benzene, and a nitrogen determination gave results agreeing with the calculated for *1-phenyl-5-methyl-3-ethoxytriazole.*

	Calculated for $C_{11}H_{13}N_3O$.	Found.
N	20.7	20.9

On the Benzoylimidothiocarbonic Esters and their Behavior with Hydrogen Chloride.

Diethyl Benzoylimidothiocarbonate, $C_6H_5CON{=}C<\begin{matrix}SC_2H_5\\OC_2H_5\end{matrix}$.—We have prepared a series of these esters by treating the potassium salts of the benzoylthioncarbamic esters, in alcoholic solution, with alkyl iodides. Warming, during this process, must be avoided, since otherwise, as found by Lössner in the case of the preparation of the diethyl ester,* mercaptan is evolved, and the oils suffer more or less decomposition with the formation of benzamide. The potassium salts of the benzoylthioncarbamic esters crystallize more readily than the sodium salts. In order to prepare them, alcoholic potash is added to a strong solution of the ester in alcohol, when a crystalline mass separates at once. On treating the potassium salt of ethyl benzoylthioncarbamate suspended in alcohol with ethyl iodide, the mixture, after standing twelve hours, no longer had an alkaline reaction. Water was then added, and the precipitated oil was extracted with ether, washed, and then thoroughly dried over calcium chloride.

* Loc. cit.

On evaporating and distilling the oil at 19 mm. pressure, the material all boiled from 209° to 212°, almost from the first to the last drop. There was no sign of decomposition, and the yield is almost quantitative, a portion being lost in treating the alcohol solution with water. Thus obtained, ethyl benzoylimidothiocarbonate is a colorless oil of a faint odor, resembling the xanthic esters. Without further purification of the oil a nitrogen determination gave:

	Calculated for $C_{12}H_{15}NO_2S$.	Found.
N	5.9	6.2

Dimethyl Benzoylimidothiocarbonate, $C_6H_5CON{=}C{<}^{SCH_3}_{OCH_3}$, was obtained when 46 g. of methyl benzoylthioncarbamate, 9.5 g. of potassium hydrate, and 33.5 g. of methyl iodide were mixed in methyl alcohol. The mixture became warm, and the odor of mercaptan was noticed; this greatly increased on attempting to distil off the methyl alcohol after the action was complete. The heating was then stopped and cold water was added, and the oil was extracted with ether, whereupon, on evaporating, 22 g. of this ester were obtained, which, on standing, deposited plates of benzamide. These were filtered, and the oil, without further purification, was used for the following experiments:

About 1 g. of the oil was dissolved in benzene and hydrogen chloride was passed in; warming and effervescence took place, and a mass of colorless needles separated, which melted at 152°–153° and were identical in every respect with *methyl benzoylthiolcarbamate*, $C_6H_5CO{-}NHCO.SCH_3$, described above.

Three g. of the oil were heated on the water-bath for about an hour and a half in a stream of hydrogen sulphide (when mercaptan (?), and some methyl alcohol condensed in the delivery tube), and, on cooling, dissolving in potassium hydrate and precipitating with hydrochloric acid, needles were obtained. When these were crystallized from dilute alcohol, they were found to be *methyl benzoylthioncarbamate*, $C_6H_5CONHCS.OCH_3$,

described above. When this oil is allowed to stand in water, it remains liquid for weeks. On exposure, the crude oil evaporated, leaving benzamide.

Benzoylimidomethylthiolethylcarbonate,

$$C_6H_5CON{=}C{<}{SC_2H_5 \atop OCH_3},$$

was prepared like the above diethyl ester. It was distilled at 20 mm. pressure, when it boiled for the most part at about 210°. It then did not solidify in a freezing-mixture, and in properties it resembled the diethyl compound. When this oil was treated in dry benzene with hydrogen chloride, it evolved methyl chloride and gave *ethyl benzoylthiolcarbamate*,

$$C_6H_5CONHCO.SC_2H_5,$$

which, on evaporating the benzene and crystallizing from dilute alcohol, separated in long, slender prisms melting from 105°–107°. It is soluble in sodium hydrate, and a nitrogen determination gave:

	Calculated for $C_{10}H_{11}NO_2S$.	Found.
N	7.0	6.7

An attempt to prepare this ester by warming ethyl thiolcarbamate, $H_2NCO.SC_2H_5$, with benzoic anhydride under conditions that were found to be favorable in the case of the corresponding acetyl compound, resulted in the formation of *cyanphenine* and a body which crystallized from alcohol in needles and melted finally at 167°–168°. This material contained sulphur, and a nitrogen determination gave results agreeing with the calculated for benzoyl rhodanide, the compound probably being the polymeric modification described by Miquel,* who states that it melts at 160°.

	Calculated for $(C_6H_5CO{-}NCS)_x$.	Found.
N	9.1	9.6

Benzoylimidomethylthiolisopropylcarbonate,

$$C_6H_5CON{=}C{<}{SC_3H_7 \atop OCH_3}.—$$

Isopropyl iodide reacts more slowly on the potassium salt

* Ann. Chim. Phys. [5], xi, 269.

of methyl benzoylthioncarbamate than the lower alkyl iodides. When 10 g. of the ester are used, it is necessary to let the mixture stand for about three or four days. When the product was treated with hydrogen chloride, it gave

Isopropyl Benzoylthiolcarbamate, $C_6H_5CONHCO.SC_3H_7$.—This crystallizes from alcohol in colorless prisms, which melt at 136°–137°. It is soluble in alkali, and a nitrogen determination gave:

	Calculated for $C_{11}H_{13}NO_2S$.	Found.
N	6.2	6.2

Benzoylimidomethylthiolisobutylcarbonate,

$$C_6H_5CON{=}C{<}^{SC_4H_9}_{OCH_3},$$

is an oil like the preceding. It required from two to three days for its preparation. When dry hydrogen chloride is led into its solution in benzene, it evolves methyl chloride and gives

Isobutyl Benzoylthiolcarbamate, $C_6H_5CONHCO.SC_4H_9$, which crystallizes from dilute alcohol in thin plates or scales and melts at 115°–117°. It is insoluble in water, but readily soluble in benzene and sodium hydrate, and a nitrogen determination gave:

	Calculated for $C_{12}H_{15}NO_2S$.	Found.
N	5.9	6.0

Benzoylimidomethylthiolisoamylcarbonate,

$$C_6H_5CON{=}C{<}^{SC_5H_{11}}_{OCH_3}.—$$

In this case the action was complete in two days, it being hastened finally by warming. The oil, without distilling, was dried in a vacuum at 100°, when a nitrogen determination indicated the presence of benzamide.

	Calculated for $C_{14}H_{19}NO_2S$.	Found.
N	5.28	6.0

On standing, some benzamide separated. When this oil was treated with dry hydrogen chloride and the material puri-

fied by means of alkali and dilute alcohol, a compound crystallizing in needles was obtained, which melted at 96°. A nitrogen determination gave results which agreed with the calculated for *methyl benzoylthioncarbamate*, the calculated being 7.1 per cent, while 6.9 per cent was found. The calculated for the expected isoamyl benzoylthiolcarbamate is 5.5 per cent. The compound obtained had all the properties of the benzoylthionmethyl ester described above. This is the first exception to the rule that thiolcarbamic esters are formed by the action of hydrogen chloride on the imidothiolcarbonates.

On the Behavior of Benzoylimidothiocarbonic Esters with Amines, and on the Behavior of Benzoylpseudoureas with Hydrochloric Acid.

As stated in the introduction, the behavior of the benzoylimidothiocarbonic esters with bases has been investigated only in the case of ammonia.* We show below that the benzoylimidothiocarbonic esters readily react also with alkyl and aryl amines giving benzoylpseudourea ethers. Attempts to purify these compounds by distillation, in certain cases, were not crowned with success. Their behavior, however, with hydrochloric acid is described as the most characteristic reaction or simple test for their presence that we have observed, since by this treatment they evolve alkyl chloride and are, in most cases, quantitatively converted into the corresponding, easily crystallizable, benzoylureas.

Benzoylpseudomethylurea, $C_6H_5CO—N{=}C{<}{NH_2 \atop OCH_3}$. — This compound was prepared from benzoylimidomethylthiolisopropyl carbonate and alcoholic ammonia by allowing the mixture of these substances to stand for twelve hours, whereupon isopropyl mercaptan separated and the compound obtained by Dixon, in a similar manner, was obtained. It melted at 77° and agreed with his description. On treating this with 20 per cent hydrochloric acid, a reaction did not start immediately, but, on gently warming, the material melted, then

* Dixon, loc. cit.

solidified, and, on crystallizing from alcohol, small lozenge-shaped plates separated, melting at 214° with effervescence. This material had all the properties of *benzoylurea*,

$$C_6H_5CONHCONH_2,$$

described above.

Benzoylpseudomethylethylurea, $C_6H_5CO{-}N{=}C{<}^{NHC_2H_5}_{OCH_3}$. — This was prepared from benzoylimidomethylthiolisopropyl carbonate by allowing a little less than 1 g. of the ester to stand for several days with a 33 per cent aqueous solution of ethylamine mixed with enough alcohol to form a solution. On then evaporating, an oil was obtained which was treated, without further handling, with 20 per cent hydrochloric acid, whereupon it was converted into

a-β-Benzoylethylurea, $C_6H_5CONHCONHC_2H_5$. — On standing, this separated from the hydrochloric acid solution in long needle-like prisms, some over 2 cm. in length. The preparation of this compound by a new method is of interest, because of the discrepancy between the melting-points recorded for this compound by Miquel,* Leuckart,† and Dixon.‡ These authors give 192°, 168°, and 114°–114.5°. On crystallizing our material from petroleum ether, it melted sharply at 114° and agreed in all respects with the compound prepared by Dixon from a,β-benzoylethylthiocarbamide by desulphurization so that evidently this is the correct melting-point for the substance.

Benzoylpseudomethylisobutylurea, $C_6HCO{-}N{=}C{<}^{NH.C_4H_9}_{OCH_3}$. — When isobutylamine is mixed with benzoylimidomethylthiolethyl carbonate, the mixture starts to boil immediately, giving off ethyl mercaptan, and cooling is necessary. The product is an oil which, when treated with hydrochloric acid, slowly gives off methyl chloride and solidifies, forming

Benzoylisobutylurea, $C_6H_5.CONHCONHC_4H_9$. — This was crystallized from alcohol, when long, slender prisms were ob-

* Ann. Chim. Phys. [5], xi, 318. † J. prakt. Chem. [2], xxi, 33.
‡ J. Chem. Soc. (London), 1899, 383.

tained, melting sharply at 115°. A nitrogen determination gave:

	Calculated for $C_{12}H_{16}N_2O_2$.	Found.
N	12.7	12.9

Benzoylpseudomethyldiisoamylurea,

$$C_6H_5CO{-}N{=}C{<}{}^{N(C_5H_{11})_2}_{OCH_3}.$$—

When benzoylimidothiolmethyl carbonate and diamylamine are mixed, reaction starts in the cold. The material was warmed to 60° until methyl mercaptan ceased being evolved, when hydrogen sulphide was passed in for several hours. On cooling, a mass of plates separated; these proved to be benzamide. On filtering and distilling at 13 mm. pressure diisoamylamine, boiling at 72°, benzonitrile, and benzamide formed the chief products. An appreciable amount of diamylthionmethylcarbamate was not obtained.

This and the corresponding ethylbenzoylpseudourea ether differ from most of the other urea ethers that we have examined by the fact that, although they give off alkyl chloride with hydrochloric acid, nevertheless, a body corresponding to benzoyldiisoamylurea was not obtained. A number of experiments were tried with hydrochloric acid under different conditions, but in every case nothing but benzamide and diisoamyl hydrochloride could be isolated. This behavior is in accordance with the ease with which the addition-product in the case of ethyl benzoylthioncarbamate and diisoamylamine gives benzamide and free amine. When ***pseudoethylbenzoyldiisoamylurea*** was prepared from benzoylimidothioethyl carbonate and diamylamine, and the product treated with hydrochloric acid, ethyl chloride was evolved, and again nothing but benzamide and amine hydrochloride was found.

Benzoylpseudomethylphenylurea, $C_6H_5CON{=}C{<}{}^{NHC_6H_5}_{OCH_3}$.—Benzoylimidomethylthiolethyl carbonate and aniline readily react when mixed, and the action may be hastened by warming on the water-bath. After the evolution of ethyl mercaptan had ceased, in one experiment, we attempted to purify the

product by distilling at 16 mm. pressure. Both the temperature and pressure rose steadily, the material beginning to boil at 70°. At this pressure, when the temperature rose to 200°, benzonitrile and other products distilled over, leaving a mass of tar in the distilling bulb.

When this crude pseudourea ether is treated with hydrochloric acid, it reacts at once, solidifying and giving off methyl chloride, and, on crystallizing the product from alcohol, benzoylphenylurea, melting at 202°–203°, is obtained. It is identical with the product obtained from ethylbenzoylthioncarbamate and aniline described above.

Benzoylpseudoethylphenylurea, $C_6H_5CO{-}N{=}C{<}^{NHC_6H_5}_{OC_2H_5}$, from 2 g. of aniline and 4.8 g. of benzoylimidothioldiethyl carbonate, formed a clear light-yellow oil, after heating for some time in a vacuum on the steam-bath. A preparation made in this manner was analyzed with the following result:

	Calculated for $C_{16}H_{16}N_2O_2$.	Found.
N	10.4	10.8

Benzoylpseudomethyl-m-chlorphenylurea,

$$C_6H_5CON{=}C{<}^{NHC_6H_4Cl}_{OCH_3},$$

was obtained from metachloraniline and benzoylimidomethylthiolethyl carbonate after eight hours' heating on the water-bath. It was converted directly by hydrochloric acid into *benzoylmetachlorphenylurea*, $C_6H_5CONHCONHC_6H_4Cl$, which crystallizes in needles from alcohol, melting at about 200°. We were unable to obtain all the nitrogen from this compound on burning with copper oxide in the usual manner. Two determinations gave 8.60 and 8.64 per cent of nitrogen, while the calculated is 10.2 per cent. In order to determine whether this peculiarity is the fault of the analytical method and whether the above compound is the benzoylurea in question, we prepared this benzoylmetachlorphenylurea by desulphurizing *benzoylmetachlorphenylthiourea*,

$$C_6H_5CONHCSNHC_6H_4Cl,$$

in regard to the structure of which there can be no question, since it was prepared from pure benzoyl rhodanide and colorless metachloraniline, the latter boiling from 229° to 231°. Here, again, we had the same difficulty on analysis; a determination gave 8.4 per cent instead of 9.6 per cent nitrogen. This material crystallizes from alcohol in colorless needles melting at 125°. On boiling the alcoholic solution of this compound with silver nitrate and a little water, a compound was obtained which crystallized in needles and melted at 200°. It was identical in every respect with the above compound obtained from the pseudourea ether, and, when portions of the two samples were mixed, the melting-point was not altered. It follows, therefore, that the material is the urea in question, and that this urea and thiourea do not give up all their nitrogen under the usual conditions of a nitrogen determination.

Benzoylpseudomethyl-m-nitrophenylurea,

$$C_6H_5CON{=}C{<}{}^{NHC_6H_4NO_2}_{OCH_3}.$$ —

After heating metanitraniline with benzoylimidomethylthiolethyl carbonate for four or five hours on the water-bath, the evolution of ethyl mercaptan ceased. The oil thus obtained was treated with hydrochloric acid, whereupon it changed to a crystalline mass. This was washed with water and crystallized from alcohol, whereupon it gave

Benzoylmetanitrophenylurea, $C_6H_5CONHCONHC_6H_4NO_2$. — This is insoluble in water and chloroform and difficultly soluble in benzene and alcohol. From the latter solution it separates in the form of fine, short needles, which melt from 231° to 232°. A nitrogen determination gave:

	Calculated for $C_{14}H_{11}N_3O_4$.	Found.
N	14.7	14.4

Benzoylpseudomethylpseudocumylurea,

$$C_6H_5CO{-}NC{=}{<}{}^{NHC_6H_2(CH_3)_3}_{OCH_3},$$

was readily formed on warming benzoylimidothiolmethyl carbonate and pseudocumidine. On cooling, the mass was

treated with hydrochloric acid, whereupon methyl chloride escaped and, on washing with water and alcohol and crystallizing from chloroform, a woolly mass of very bulky, long needles was obtained. This substance melted at 207°, and on analysis proved to be

Benzoylpseudocumylurea, $C_6H_5CONHCONHC_6H_2(CH_3)_3$.

	Calculated for $C_{17}H_{18}N_2O_2$.	Found.
N	9.92	9.78

Benzoylimidomethylthiolisobutyl carbonate and methylaniline reacted very slowly, giving off mercaptan. After warming on the water-bath for three days, an oil was obtained that had a beautiful purple color. It did not readily solidify with hydrochloric acid, and, therefore, it was not further examined.

New Haven, April 30, 1900.

ON THE MOLECULAR REARRANGEMENT OF DISUBSTITUTED THIONCARBAMIC ESTERS: PHENYLIMIDOTHIOCARBONIC ACID DERIVATIVES AND THIOSEMICARBAZIDIC ESTERS.*

By HENRY L. WHEELER AND GUY K. DUSTIN.

In previous articles from this laboratory it has been shown that monosubstituted thioncarbamic esters, XNHCS.OR, react more or less readily with alkyl iodides, giving the isomeric thiol derivatives, XNHCO.SR; and it was concluded that these ester amides are best represented by the normal form rather than by the pseudo structure, $XN{=}C{<}^{SH}_{OR}$. It seemed desirable, however, to determine whether or not the above-mentioned rearrangements were dependent on the presence of hydrogen; or, in other words, whether disubstituted xanthogenamides of the form XX'N—CS.OR would undergo a similar rearrangement, giving the thiol derivatives, the question being all the more interesting since it is customary to represent the thioamides and thioureas as reacting in their pseudoform with halogen compounds.

We find that the disubstituted thioncarbamic esters readily react with alkyl iodides, and that the N-methyl (1) and ethylthioncarbanilic esters undergo a rearrangement even more readily than the thioncarbanilic esters of the form $C_6H_5NHCS.OR$. It follows, therefore, that the pseudoform is not involved in these reactions, and that the rearrangement takes place, in general, as follows:

I.

$$\begin{matrix}CH_3\\C_6H_5\end{matrix}{>}N{-}CS.OCH_3 \rightarrow \begin{matrix}CH_3\\C_6H_5\end{matrix}{>}N{-}C{=}S{\begin{matrix}\diagup CH_3\\-I\\ \diagdown OCH_3\end{matrix}} \rightarrow$$

$$\begin{matrix}CH_3\\C_6H_5\end{matrix}{>}N{-}CO.SCH_3.$$

* Amer. Chem. Jour., xxiv, No. 5.

It is easy to distinguish whether a rearrangement has taken place or is complete in this series, since the thion derivatives are readily desulphurized by mercuric oxide when boiled in alcoholic solution, while the thiol derivatives are unaffected. The action takes place smoothly as follows:

II.

$$CH_3.C_6H_4NCS.OR \rightarrow CH_3.C_6H_4NCO.OR.$$

It was shown by Liebermann* that the sodium and silver salts of the thioncarbanilic esters react with allkyl halides in the following manner:

III.

$$C_6H_5N{=}C\begin{matrix} \diagup SAg \\ \diagdown OC_2H_5 \end{matrix} \rightarrow C_6H_5N{=}C\begin{matrix} \diagup SC_2H_5 \\ \diagdown OC_2H_5 \end{matrix}.$$

Thus, the alkyl group attaches itself to sulphur, and phenylimidothiocarbonic esters result. He examined the action of these compounds with sulphuric acid, aniline, and ammonia, at high temperatures. He found that the action of sulphuric acid gave aniline sulphate and thiocarbonic esters, thus showing the constitution of the compounds. With aniline, mercaptan was given off and carbanilide separated, while with ammonia (at 100°) decomposition products alone were obtained. He states that with hydrochloric acid alkyl chloride is evolved, on warming, and the compounds are converted back into phenylsulphurethane.

We have prepared some of these compounds in order to compare their behavior with that of the analogous acylimidothiocarbonic esters, $C_6H_5CO{-}N{=}C{<}^{SC_2H_5}_{OC_2H_5}$, and with that of anilinoimidothiocarbonic ester, the hydrazone of diethyl thiocarbonate, $C_6H_5NH{-}N{=}C{<}^{SC_2H_5}_{OC_2H_5}$. The results of the comparison show how strikingly the properties of compounds of similar structure are influenced by the character of groups.

It has been found that the benzoylimidothiocarbonic esters

* Ann. Chem. (Liebig), ccvii, 148.

readily react with organic bases,* while the hydrazone of ethyl thiocarbonate, which has precisely opposite properties, readily and smoothly reacts only with negative compounds, such as acyl chlorides, hydrochloric acid, thiobenzoic acid, etc.† We now find that the phenylimidothiocarbonic esters exhibit a behavior intermediate between the above, inasmuch as they are surprisingly unreactive with both acyl chlorides and with organic bases; in fact, they show a wide departure from most compounds which contain the imido-ester grouping.

For example, it might be expected that the compounds of Liebermann would react with bases, giving the pseudourea ethers of Stieglitz and Dains.‡ It was found, however, that aniline acts on these compounds only near its boiling-point, and then very slowly, and that carbanilide separates from the hot mixture, in crystalline form, before one-half of the mixture enters into reaction. On distilling, no pseudourea ether was found.

The hydrazone of thioethyl carbonate, like the isoanilides in general, reacts with acetyl and benzoyl chloride, in the cold, with a violent evolution of alkyl chloride, while the compounds of Liebermann can be mixed with these chlorides without any evidence of reaction. Benzoyl chloride showed no signs of reacting with the following ester below 140°. On long-continued heating, above this temperature, methyl chloride was slowly evolved and a benzoyl derivative was obtained. The reaction, in all probability, took place as follows:

IV.

$$C_6H_5N{=}C{<}\begin{matrix}SCH_3\\OCH_3\end{matrix} + Cl.COC_6H_5 = \begin{matrix}C_6H_5{-}N{-}CO.SCH_3\\ \quad\;\; | \\ \quad C_6H_5CO\end{matrix} + CH_3Cl.$$

This action is probably analogous to that of hydrogen chloride, with which reagent the phenylimidothiocarbonic esters react smoothly and quantitatively, like the imidothiocarbonic esters in general, giving thiolcarbamic esters and not, as Lie-

* Wheeler and Johnson, Amer. Chem. Jour., xxiv, 189.

† Wheeler and Barnes, Ibid., xxiv, 60.

‡ Jour. Amer. Chem. Soc., xxi, 136.

bermann states, regenerating phenylsulphurethane or the thion derivative. This mistake of Liebermann is probably due to the fact that ethyl thioncarbanilate and the corresponding thiol compound differ by about 1° in their melting-points, and may be easily mistaken for each other. However, the other members of these series differ more widely in their melting-points. The reaction with hydrogen chloride takes place with the formation of an addition-product, which decomposes with loss of alkyl chloride, as follows:

V.

$$C_6H_5N{=}C{<}\substack{SC_2H_4\\OC_2H_4} \rightarrow C_6H_4\overset{H}{N}{-}C\substack{\diagup SC_2H_5\\ -Cl \\ \diagdown O\,C_2H_5}$$

In these and similar compounds it is almost invariably the group attached to oxygen that is evolved as alkyl chloride, and a thiol ester is formed. As another example of the comparative inertness of the phenylimidothiocarbonic acid grouping, we may add that no reaction was observed when benzoyl chloride was mixed with the silver salt of methyl thioncarbanilate suspended in benzene; and when the mixture was heated to 100°, benzanilide was obtained.

With acetyl chloride the salt reacts in the cold. Silver chloride and an acetyl derivative are obtained as follows:

VI.

$$C_6H_5N{=}C{<}\substack{SAg\\OCH_3} \rightarrow \substack{CH_3CO\\C_6H_4N}{>}N{-}C\substack{\diagup S\,Ag\\ -Cl \\ \diagdown OCH_3}$$

$$\substack{CH_3CO\\C_6H_5}{>}N{-}CS.OCH_3.$$

With the object of obtaining a new type of thiocarbamic esters, which perhaps may be called acylsulphosemicarbazidic esters, *i. e.*, $C_6H_5CONHCSN(C_6H_5){-}NHCSOR$, etc., since they contain the sulphosemicarbazide grouping,

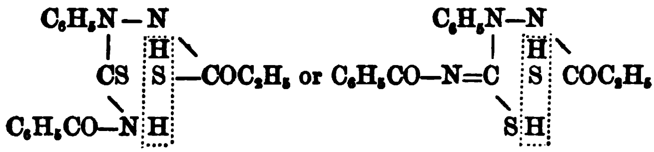
$$-NH-CS-\overset{|}{N}-NH-,^{*}$$

* For convenience in naming these compounds, sulphur in the urea radical is termed sulpho; when in the ester grouping, it is called thion or thiol; and for general reference the compounds are referred to as thiosemicarbazidic esters.

we examined the behavior of acetyl and benzoylsulphocyanides with ethyl phenylthiocarbazinates. It was found that the thion ester behaves in a different manner from that of the thiol ester.

When acetyl- or benzoylsulphocyanide is mixed with ethyl phenylthioncarbazinate, hydrogen sulphide is evolved, even in the cold, and compounds of a very stable nature result. The reaction evidently takes place first by addition, with the formation of ethyl *c*-benzoyl-*b*-phenylsulpho-*a*-thionsemicarbazidate. This probably takes place according to one of the two following schemes, and hydrogen sulphide then separates as shown by the dotted lines, giving ring-formed compounds which are either triazole (VII) or thiobiazolone derivatives (VIII):

VII. VIII.



Which ring is formed depends on whether the intermediate addition-product has the structure of a normal (VII) or pseudosulpho (VIII) semicarbazidic ester.

Freund and König* represent the action of isocyanphenyl chloride, $C_6H_5N{=}CCl_2$, on acylhydrazines in the same manner as that of phosgene, the products being viewed as imidoxybiazolines or compounds analogous to VIII. The action in the present case might be expected to be similar. On the other hand, it has been shown by Marckwald† that compounds of this type are not desulphurized by metallic oxides while our material is desulphurized by silver nitrate; therefore, at present, we are inclined to represent these compounds as triazole derivatives, and assume the action to proceed as shown in VII.

When acetyl- or benzoylsulphocyanide is mixed with ethyl phenylthiolcarbazinate, no hydrogen sulphide is evolved, but

* Ber. d. chem. Ges., xxvi, 2869. † Ibid., xxv, 3109; xxvii, 617.

the compounds unite directly to form an addition-product, as follows:

IX.

$$C_6H_5CONCS + C_6H_5NH{-}NHCO.SC_2H_5 = C_6H_5CONHCSN(C_6H_5){-}NHCO.SC_2H_5.$$

These reactions sharply distinguish the thion- from the thiol-carbazinic esters, and the ease with which the former give ring compounds seems to indicate that the thion derivatives have the pseudo form. However, other facts, such as special arrangement, must also be considered in these cases.

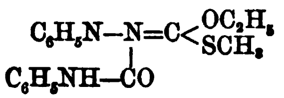
That the above formation of triazole derivatives (VII) is probably not caused by the phenylthioncarbazinic ester having the pseudo form is shown by the behavior of the latter with phenyl isocyanate. These compounds combine directly without giving off hydrogen sulphide, and the product has the composition of the expected ethyl *c,b*-diphenyl-*a*-thionsemicarbazidate:

X.

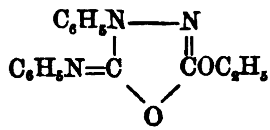
$$C_6H_5NCO + C_6H_5NH{-}NHCS.OC_2H_5 = C_6H_5NHCON(C_6H_5){-}NHCS.OC_2H_5.$$

That the addition takes place to the nitrogen to which the phenyl group is attached, and that the grouping $-NHCS.OC_2H_5$ is present, is shown by the behavior of the compound with alkali and alkyl iodides. With methyl iodide and sodium methylate in the cold, diphenylureaimidothiolmethylethyl carbonate, the diphenylsemicarbazone of thiolmethylethyl carbonate, is formed (XI); while under the same conditions ethyl iodide gives a mixture of two compounds. These are thioldiethylcarbonicesterdiphenylsemicarbazone analogous to XI and a substance, free from sulphur, which appears to be the ring-formed compound *α*-ethoxy-*α*′-phenylimido-*β*′-phenyloxybiazoline (XII):

XI.



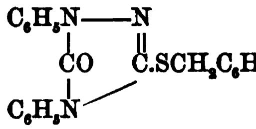
XII.



The compound XII is also formed on simply warming the diphenylthionsemicarbazidic ester with sodium ethylate.

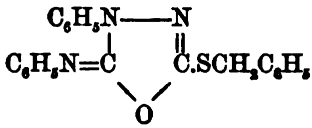
On the other hand, with benzyl chloride the sole product obtained was not strictly analogous to either of the above derivatives; it contained sulphur, and agreed in composition with one of the following compounds:

XIII.



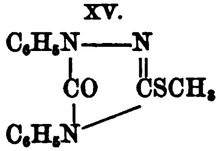
or

XIV.

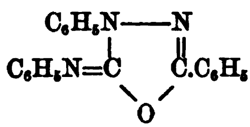


At present we have nothing but the properties of the compound to indicate to which of these series it belongs. The structure represented by formula XIII appears to be excluded, since Marckwald* has prepared a compound of this type, namely, 1-4-diphenyltriazolone-3-methylmercaptan (XV), and he has shown that this substance has decided basic properties, that it is soluble in acids, and that it gives a platinum double salt. Our compound, on the other hand, has no basic properties whatever. The nearest known analogues of a compound represented by formula XIV are the phenylimidooxybiazolines prepared by Freund and König.† The properties of their "*n*-phenyl-phenyl-phenylimidooxybiazolin" (α-phenyl-α'-phenylimido-β-phenyloxybiazoline, XVI) are closely similar to those of our compound, inasmuch as it is insoluble in water and is not affected by boiling with soda or hydrochloric acid, in which it is also insoluble:

XV.



XVI.



Moreover, it was found that the compound free from sulphur, mentioned above, has no basic properties, and therefore

* Ber. d. chem. Ges., xxv, 3111. † Loc. cit.

it appears that formulas XII and XIV best represent the structure of the compounds in question. Further work on the structure of these compounds must be deferred to a later date, owing to the departure of one of us from this laboratory.

The behavior of the diphenylthionsemicarbazidic ester (X) with bases showed a wide departure from that of the benzoylthioncarbamic esters, since derivatives of the pseudourea type were not obtained. When heated with aniline, or in fact when heated alone, carbanilide is the chief product. The properties of this type of esters are most closely related to those of the thioncarbanilic esters.

When the diphenylsemicarbazones of the thiolcarbonic esters (XI) are treated with hydrogen chloride, a reaction similar to that described in the case of the phenylimidothiocarbonic esters takes place (V above). The compounds obtained are identical with those prepared by adding phenyl isocyanate to the phenylthiolcarbazinic esters, in which case again no hydrogen sulphide is evolved; the addition therefore takes place in a similar manner to that shown in X.

In addition to the above we have investigated the action of some thion and thiol salts of carbonic and carbamic acids with ethyl chlorcarbonate, and we find that no two of these salts behave alike. For example, Bender's salt, to which the structure $C_2H_5OCO.SK$ is assigned, reacts in two ways as follows, chiefly according to XVII:

XVII.

$$C_2H_5OCO.SK + ClCO.OC_2H_5 = C_2H_5OCO.OC_2H_5 + KCl + COS.$$

XVIII.

$$C_2H_5OCO.SK + ClCO.OC_2H_5 = C_2H_5O.CO.SC_2H_5 + KCl + CO_2.$$

The products are diethyl carbonate, diethylthiol carbonate, carbon oxysulphide, carbon dioxide, and potassium chloride.

Potassium xanthate, $C_2H_5OCS.SK$, reacts with 1 molecule of chlorcarbonic ester in an extremely complicated manner. We identified the presence of five different oils in the reaction-product. These were carbon disulphide, ethyl carbonate,

diethyl thioncarbonate, xanthogenic ester, and Welde's * "disulphodicarbothionsäurediäthyl ester."

We were unable to obtain the sodium salt of thionethyl carbonate, $C_2H_4OCS.ONa$, described by Klason.† In this respect our experience coincides with that of Bergreen,‡ whose results on the action of thiophosgene on sodium ethylate we are able to confirm.

Ammonium dithiocarbanilate, $C_6H_5NHCS.SNH_4$, gave, with 1 molecule of chlorcarbonic ester, chiefly thiocarbanilide, phenylsulphocarbamide, and phenyl mustard oil; while the phenylhydrazine salt of dithiophenylcarbazinic acid,

$$C_6H_5NH—NHCSSH.H_2N—NHC_6H_5,$$

gave a good yield of Heller's § ethyl phenylcarbazinate. The latter had all the properties mentioned by Widman.‖ Besides this, an unpromising green tar was formed.

Experimental Part.

Methyl Methylthioncarbanilate, $\genfrac{}{}{0pt}{}{CH_3}{C_6H_5}>N—OS.OCH_3$.—The chloride, $C_6H_5(CH_3)NCS.Cl$, was prepared by the method of Billeter.¶ In two experiments 15 g. of thiophosgene gave the theoretical yield of the chloride. This was added to a solution of sodium methylate in methyl alcohol, when a reaction took place at once; it was warmed for a half hour on the water-bath, then treated with water, extracted with ether, and distilled at 19 mm. pressure, whereupon it boiled mostly from 151° to 152°. It was a colorless oil which did not solidify on cooling, and a nitrogen determination gave:

	Calculated for $C_9H_{11}NOS$.	Found.
N	7.7	7.3

Methyl Methylcarbanilate, $C_6H_5(CH_3)NCO.OCH_3$, was formed on boiling the above thion ester (12 g.) with an excess of mercuric oxide in alcoholic solution. It was obtained as an

* J. prakt. Chem. [2], xv, 45.

† Ber. d. chem. Ges., xx, 2384.

‡ Ibid., xxi, 346.

§ Ann. Chem. (Liebig), cclxiii, 278.

‖ Ber. d. chem. Ges., xxviii, 1927.

¶ Ibid, xx, 1631.

oil which distilled for the most part from 117° to 119° at 16 mm. pressure, and a nitrogen determination gave:

	Calculated for $C_9H_{11}NO_2$.	Found.
N	8.48	8.71

Ethyl Methylthioncarbanilate, $C_6H_5(CH_3)NCS.OC_2H_5$.—This was prepared from the above chloride in the same manner as the methyl ester. It formed a colorless oil which boiled mostly from 145° to 150° at 18 mm. pressure. It refused to solidify, and a nitrogen determination gave:

	Calculated for $C_{10}H_{13}NOS$.	Found.
N	7.1	6.9

It may be boiled with concentrated hydrochloric acid without change.

Methyl N-Ethylthioncarbanilate, $C_6H_5(C_2H_5)NCS.OCH_3$.—This compound was prepared in the same manner as the corresponding ethyl ester.* The crude product was obtained as an oil which was distilled at 18 mm. pressure, whereupon the most of the material boiled from 148° to 149°. It then solidified and, on crystallizing from petroleum ether, beautiful, colorless, five-sided plates separated, melting from 41° to 42°. A nitrogen determination gave:

	Calculated for $C_{10}H_{13}NOS$.	Found.
N	7.17	7.50

Methyl Methylthiolcarbanilate, $C_6H_5(CH_3)NCO.SCH_3$.—This compound is easily obtained when the thion ester is heated with methyl iodide for four hours from 103° to 106°. On cooling, a small amount of crystalline material separates, which appears to be trimethylphenylammonium iodide. The rest of the product, when distilled at 16 mm. pressure, boils for the most part from 140° to 142°. The material then solidifies, and when crystallized from alcohol, in which it is readily soluble, it melts at 46°. It forms colorless plates which, on analysis, gave:

* Billeter and Strohl, Ber. d. chem. Ges., xxi, 104.

	Calculated for $C_9H_{11}NOS$.	Found.
N	7.77	7.38

This ester has been obtained in another manner by Bertram.* He states that it melts at 54°. Our material was free from the thion ester, since it was not desulphurized on boiling with mercuric oxide.

Ethyl N-Methylthiolcarbanilate, $C_6H_5(CH_3)NCO.SC_2H_5$.—The thion ester was heated in a closed tube for a number of hours at 100° with ethyl iodide; then, on distilling, an oil was obtained which boiled from 160° to 163° at 19 mm. pressure. On cooling, this solidified and melted at about 12°–13°. A nitrogen determination gave:

	Calculated for $C_{10}H_{13}NOS$.	Found.
N	7.17	7.38

Methyl N-Ethylthiolcarbanilate, $C_6H_5(C_2H_5)NCOSCH_3$.—This was obtained as an oil by heating the thion ester with methyl iodide. It boiled from 148° to 149° at 17 mm. pressure, and it did not solidify on cooling. A nitrogen determination gave results agreeing with the calculated. The record of this determination is lost. It was free from the thion ester, since it was not desulphurized by boiling in alcoholic solution with mercuric oxide.

Ethyl N-Dimethylthioncarbamate, $(CH_3)_2NCS.OC_2H_5$.—The action of alcoholic dimethylamine was tried on xanthogenic ester in order to see if the action in the case of aliphatic amines is the same as that of ammonia and phenylhydrazine. It was found that these substances react less smoothly than when ammonia is used. In the present case, after the above mixture was allowed to stand about two weeks, the product was an oil which distilled, for the most part, at 203°–205°. A nitrogen determination indicated the presence of xanthogenic ester. The material was then treated with alcoholic potash and allowed to stand for twenty-four hours, whereupon, on

* Ber. d. chem. Ges., xxv, 53.

distilling, it boiled from 205° to 206°, and a nitrogen determination gave 9.1 per cent of nitrogen instead of 10.5.

Diamylamine reacted even less smoothly with xanthogenic ester. When these substances were mixed and allowed to stand for four or five days, then heated for some time on the steam-bath, mercaptan was given off, but the product, when distilled, gave no constant boiling-point.

Dimethyl Phenylimidothiolcarbonate, $C_6H_5N{=}C{<}^{SCH_3}_{OCH_3}$.—This was prepared by treating methyl thioncarbanilate in methyl alcohol with sodium methylate and methyl iodide. On distilling, the product boiled at 133° at 17 mm. pressure and was a yellow oil with a peculiar odor. When this was treated with hydrogen chloride in solution in benzene, no precipitate was obtained, the solution evolved heat, and methyl chloride escaped. On evaporation, an oil was obtained which solidified to a mass of colorless crystals, and when crystallized from petroleum ether, fine, long needles were obtained, melting from 83° to 84°. This material was identical in every respect with *methyl thiolcarbanilate*, $C_6H_5NHCO.SCH_3$. The thion ester melts at 97°.*

When the above imidothiolcarbonic ester was heated with aniline in an oil-bath at 180°–190° for several hours, carbanilide crystallized out from the hot mixture. The heating was then stopped and the mass filtered and the oil distilled at 17 mm. pressure, whereupon about one-half of the product boiled from 82° to 131°, and the remainder from 131° to 140°. It follows from this that little or no methylisocarbanilide was present, since the isourea ethers boil near 200° at the above pressure.† On heating this carbonic ester derivative with diisobutylamine for several hours in an oil-bath from 145° to 150° no effervescence took place and little or no mercaptan was evolved. This deportment with bases is in striking contrast with the behavior of the benzoylimidothiocarbonic acid derivatives which readily react at a much lower temperature.‡

* Orndorff and Richmond, Amer. Chem. Jour., xxii, 462.

† Stieglitz, also Dains, loc. cit.

‡ Wheeler and Johnson, Amer. Chem. Jour., loc. cit.

Methyl Benzoylthiolcarbanilate, $C_6H_5CO(C_6H_5)N{-}COSCH_3$. —On mixing 2 g. of the above dimethyl carbonate with 1 molecular proportion of benzoyl chloride and heating, no action was observed below 140°. At this temperature methyl chloride was evolved, and on maintaining the bath at 150° for several hours a slow evolution of gas was noticed. On cooling and crystallizing the residue from petroleum ether, well-crystallized needles or prisms were obtained, melting at about 93°. When this was mixed with methyl thioncarbanilate (melting-point, 97°), the mixture melted at about 83°. A nitrogen determination gave:

	Calculated for $C_{15}H_{13}NO_2S$.	Found.
N	5.16	5.75

That this material is a benzoyl derivative was shown by warming it with aniline on the water-bath, when benzanilide was obtained.

When dimethylphenylimidothiol carbonate was mixed with acetyl chloride, no action whatever was observed, while the analogous ethylphenylimido-formate, $C_6H_5N{=}CHOC_2H_5$ reacts violently with acetyl chloride.*

Methyl Acetylthioncarbanilate, $CH_3CO.(C_6H_5)NCS.OCH_3$.—The silver salt of methyl thioncarbanilate was prepared in the usual way by means of sodium hydrate and alcoholic silver nitrate. It forms an amorphous gray precipitate. When this (17 g.), after drying, was treated with acetyl chloride in benzene, a reaction took place in the cold, and on evaporating the benzene and crystallizing the residue from dilute alcohol, colorless crystals separated, melting at 47°–49°. A nitrogen determination gave:

	Calculated for $C_{10}H_{11}NO_2S$.	Found.
N	6.69	6.71

The material was desulphurized on boiling in alcoholic solution with mercuric oxide, showing the presence of the thion

* Wheeler and Walden, Amer. Chem. Jour., xix, 134.

group. When this compound was warmed with aniline, it gave methyl thioncarbanilate and acetanilide.

Diethyl Phenylimidothiolcarbonate, $C_6H_5N{=}C{<}{}^{SC_2H_5}_{OC_2H_5}$.—We prepared this ester according to the directions of Liebermann,* except that alcoholic solutions were used instead of aqueous, as otherwise it frequently happens that a product is obtained which is completely decomposed when distilled. This ester was found to boil from 157° to 160° at 21 mm. pressure.

When this oil was treated with hydrogen chloride in benzene, no precipitate was obtained. On evaporating and crystallizing the residue from dilute alcohol, needles separated which melted at about 69°. That this material was ethyl thiolcarbanilate, and not the thion compound, was shown by mixing a portion with each of these substances. When mixed with the thiol ester melting from 69° to 70°, the mixture melted unaltered at the same temperature; when mixed with the thion ester melting at about 71°, it melted below 60°.

Phenylimidothiolisoamylethyl carbonate, $C_6H_5N{=}C{<}{}^{SC_5H_{11}}_{OC_2H_5}$.—This oil was prepared by Mr. T. B. Johnson in order to compare its behavior towards hydrogen chloride with that of the analogous compound, $C_6H_5CON{=}C{<}{}^{SC_5H_{11}}_{OC_2H_5}$, which latter gives a thion and not the thiol ester. The oil was made by treating the sodium salt of ethyl thioncarbanilate in alcohol with amyl bromide. When the mixture no longer gave an alkaline reaction, water was added, and the product extracted with ether. On attempting to distil the oil under reduced pressure, it decomposed. A portion of the crude material was saturated in benzene with hydrogen chloride, whereupon, on evaporating and crystallizing the residue from alcohol, long, colorless needles were obtained which melted at 66° and had all the properties of isoamyl thiolcarbanilate.

Action of Acetyl rhodanide on Ethyl Phenylthioncarbazinate.—2 g. of the latter and 1 g. of the former were mixed

* Ann. Chem. (Liebig), ccvii, 150.

together and gently warmed, whereupon hydrogen sulphide was evolved; when this ceased and the product was crystallized from 95 per cent alcohol, bunches of colorless needles separated, which melted at 93°–94°. A nitrogen determination gave the following result:

	Calculated for $C_{12}H_{13}N_3O_2S$.	Found.
N	15.96	16.54

For reasons stated in the introduction, this product is in all probability 1-phenyl-3-ethoxy-4-acetyl-5-sulphotriazolone.

Action of Benzoylrhodanide on Ethyl Phenylthioncarbazinate. — 2 g. of the carbazinic ester were mixed with 1.4 g. of the rhodanide and warmed, after hydrogen sulphide ceased being evolved, the product was crystallized from alcohol, whereupon flattened prisms melting from 136° to 138°, were obtained. These, on analysis, gave:

	Calculated for $C_{17}H_{15}N_3O_2S$.	Found.
N	12.9	12.6

The analytical result agrees with the calculated for 1-phenyl-3-ethoxy-4-benzoyl-5-sulphotriazolone. This compound is exceedingly stable, since it was found that it can be boiled with hydrochloric acid, concentrated ammonia, strong potash, aniline; and also with benzoyl chloride and be recovered unaltered. An alcoholic solution of silver nitrate desulphurizes it on boiling, which fact indicates that the substance is a triazole derivative and not a biazolone.

c-Acetylsulpho-b-phenyl-a-semicarbazidicthiolethyl Ester, $CH_3CONH—CS—N(C_6H_5)—NHCO.SC_2H_5$. — When 1 g. of thiolphenylcarbazinic ethyl ester was mixed with 0.5 g. of acetylrhodanide in benzene solution and the whole was warmed, no hydrogen sulphide was noticeable. On standing, long prisms separated, melting at 145°. These were difficultly soluble in benzene, and an analysis gave:

	Calculated for $C_{12}H_{15}N_3O_2S_2$.	Found.
N	14.14	14.28

When this product is heated to 160°, mercaptan is evolved.

c-Benzoylsulpho-b-phenyl-a-semicarbazidicthiolethyl Ester, $C_6H_5CONH—CS—N(C_6H_5)—NHCO.SC_2H_5$. — Benzoylrhodanide and ethyl thiolphenylcarbazinate readily combine in benzene solution. The product separates from benzene in colorless needles or prisms melting at 148°–150°. A nitrogen determination gave:

	Calculated for $C_{17}H_{17}N_3O_2S_2$.	Found.
N	11.69	12.13

c, b-Diphenyl-a-semicarbazidicthionethyl Ester, $C_6H_5NH—CO—N(C_6H_5)—NHCS.OC_2H_5$. — Ethyl thionphenylcarbazinate dissolves in the calculated quantity of phenyl isocyanate, when the mixture is gently warmed, and then solidifies. On crystallizing the material then from alcohol, colorless prisms, melting from 114° to 115°, separate. Nitrogen determinations gave the following results:

	Calculated for $C_{16}H_{17}N_3O_2S$.	Found. I.	Found. II.
N	13.0	13.09	13.01

When this material was heated with aniline, carbanilide was obtained which was identified by its properties and also by a nitrogen determination.

c-b-Diphenyl-a-semicarbazidicthiolethyl Ester, $C_6H_5NH—CO—N(C_6H_5)—NHCO.SC_2H_5$, formed by adding phenyl isocyanate to the thiolcarbazinic ester, crystallizes in small, spear-shaped plates, which are quite difficultly soluble in alcohol and which melt at 156°. A nitrogen determination gave:

	Calculated for $C_{16}H_{17}N_3O_2S$.	Found.
N	13.0	13.2

These esters are soluble in alkali and on boiling are decomposed.

c, b-Diphenyl-a-semicarbazidicthiolmethyl Ester, $C_6H_5NHCO—N(C_6H_5)—NHCO.SCH_3$. — This was prepared in a similar manner to the above ethyl

ester in order to determine whether it could be converted into the "diphenylimidobiazolonyl-μ-methylsulfid" (1,4-diphenyltriazolone-3-methylmercaptan) of Marckwald,* the nearest analogue of the ring-formed compounds described in this paper, and thus decide whether the compounds in question are triazol derivatives or thiobiazolones. Theoretically, all that is required is the removal of water from the above ester in the same manner as hydrogen sulphide separates in formula VII, but attempts to do this were without success. The ester crystallizes from alcohol in small plates, which melt at 186°, and it is identical with the compound prepared from diphenylurea-imidothiolmethylethyl carbonate (see below) and hydrogen chloride. When heated to its melting-point, it decomposes, slowly giving off mercaptan and phenyl isocyanate. It dissolves in concentrated sulphuric acid and is precipitated unaltered by water. It can be boiled with acetic anhydride, from which it crystallizes unaltered in prisms. It is insoluble in concentrated boiling hydrochloric acid, but it dissolves readily in alkali. When the alkaline solution was boiled, an inflammable gas was given off and, on cooling, needles separated. These melted at 161°, after crystallization from alcohol, and were insoluble in hydrochloric acid. This was not the compound sought for, and therefore it was not further examined.

c, b-Diphenyl-a-semicarbazidicthiolbenzyl Ester,

$C_6H_5NHCO{-}N(C_6H_5){-}NHCO.SCH_2C_6H_5$, — Phenyl isocyanate unites readily with thiolphenylcarbazinic-benzyl ester in benzene solution. The product is readily soluble in benzene and hot alcohol, difficultly soluble in cold alcohol, and insoluble in water. It crystallizes in small bunches of flattened prisms or plates, which melt at about 150°. A nitrogen determination gave:

	Calculated for $C_{21}H_{19}N_3O_2S$.	Found.
N	11.1	10.8

* Ber. d. chem. Ges., xxv, 3111.

Thiolmethylethylcarbonicesterdiphenylsemicarbazone,

$$C_6H_5NH-CO-N(C_6H_5)-N=C<^{SCH_3}_{OC_2H_5},$$

was prepared by adding ice-cold sodium methylate and methyl iodide to the above diphenylsemicarbazidicthionethyl ester. After remaining in the cold for two hours the action was complete, whereupon water was added, and the product extracted with ether. On crystallizing from alcohol, lozenge-shaped crystals were obtained which melted at 108°–109°, and a nitrogen determination gave:

	Calculated for $C_{17}H_{19}N_3O_2S$.	Found.
N	12.7	12.6

When this substance, dissolved in benzene, was treated with hydrogen chloride, ethyl chloride was evolved, and the above-described thiolmethyl ester, which melts at 186°, was obtained.

Thioldiethylcarbonicesterdiphenylsemicarbazone,

$$C_6H_5NHCON-(C_6H_5)-N=C<^{SC_2H_5}_{OC_2H_5},$$

was obtained when a mixture of ethyl bromide, sodium ethylate, and the above thionsemicarbazidicethyl ester was allowed to stand at ordinary temperatures for several hours. On crystallizing the product from dilute alcohol, needles were obtained which melted at about 111°. The yield is poor, as under these conditions a compound free from sulphur is also formed. The compound melting at 111° gives the above-described ethyl thiolsemicarbazidate with hydrogen chloride, a reaction which easily serves to identify it. It is readily soluble in alcohol and benzene, difficultly in petroleum ether, and insoluble in water.

a-Ethoxy-a-phenylimido-β'-phenyloxybiazoline,

$$\begin{array}{l} \quad\quad\quad\; C_6H_5N\text{——}N \\ \quad\quad\quad\quad\;\; | \quad\quad\quad \| \\ C_6H_5N=C-O-COC_2H_5 \end{array} .—$$

This appears to be the compound free from sulphur that accompanies the above carbonic ester derivative. It was also obtained when 2 g. of *c,b*-diphenyl-*a*-semicarbazidicthionethyl

ester was boiled in alcohol with sodium ethylate for two hours. Water then precipitated the compound, which crystallized in fine, long, slender prisms from alcohol. It melted at 86°, and a nitrogen determination gave:

	Calculated for $C_{16}H_{15}N_3O_2$.	Found.
N	14.9	14.6

a-Benzylmercapto-a'-phenylimido-β'-phenyloxybiazoline,

$$\begin{array}{l} \qquad\qquad\quad C_6H_5N\text{——}N \\ \qquad\qquad\qquad\;\; | \qquad\quad \| \\ C_6H_5N{=}C{-}O{-}CSCH_2C_6H_5 \end{array} .—$$

When the above diphenylsemicarbazidicthionethyl ester is dissolved in aqueous alkali and warmed with benzyl chloride, an oil is obtained which, on cooling, solidifies. On crystallizing from alcohol, the material separates in the form of colorless needles melting at 110°–112°. This contains sulphur, and nitrogen determinations gave:

	Calculated for $C_{21}H_{17}N_3OS$.	Found. I.	II.
N	11.6	11.5	11.5

This compound is insoluble in boiling water and hydrochloric acid, concentrated or dilute. It is insoluble and gives off no mercaptan on boiling with strong potash. The properties have nothing in common with Marckwald's 1, 4-diphenyltriazolone-3-methylmercaptan, and therefore they indicate that this compound is not a triazol derivative. When the substance is heated with phosphorus pentachloride, hydrogen chloride is evolved, indicating decomposition.

The Behavior of Bender's Salt, $C_2H_5OCO.SK$, with Ethyl Chlorcarbonate.—When 55 g. of the salt were treated with the calculated quantity of ethyl chlorcarbonate, the latter being dropped slowly on the salt, an energetic reaction took place and carbon dioxide and carbon oxysulphide were evolved. The latter was identified by standing over water, when hydrogen sulphide was formed. On distilling the product it boiled from 125° to 217° (?). The greater portion came over from 125° to 144°; this, when redistilled, gave 20 g. of oil boiling at

about 126°, which proved to be ethyl carbonate. The higher-boiling portions gave urethane, carbamide, and mercaptan when treated with alcoholic ammonia, indicating the presence of thiolethyl carbonate.

Potassium Xanthate, $C_2H_5OCS.SK$, and Ethyl Chlorcarbonate.—When 55 g. of potassium xanthate and 37 g. of ethyl chlorcarbonate were allowed to react and the gas that was evolved was passed into alcoholic potash, no test for carbon oxysulphide was obtained. It appeared to consist entirely or, at any rate for the most part, of carbon dioxide. On distilling the resulting oil, 5 g. boiling below 161°, 31 g. from 161° to 181°, and 10 g. from 181° to 186° were collected.

It was found on redistilling these fractions that they boiled through a much wider range and that no definite boiling-point could be obtained. In the first portions, carbon disulphide (45°–120°) and ethyl carbonate (126°–130°) were identified. On treating portions boiling from 130° to above 200° with alcoholic ammonia, ammonium sulphocyanide, ammonium carbonate, ammonium sulphide, and xanthogenamide were obtained, thus indicating the presence of thionethyl carbonate, xanthogenic ester, and Welde's * compound, $S(CS.OC_2H_5)_2$.

Ammonium Dithiocarbanilate, $C_6H_5NHCS.SNH_4$, and Ethyl Chlorcarbonate.—When the dry salt was treated with chlorcarbonic ester in molecular proportions, an energetic reaction took place, carbon oxysulphide was evolved, and a semi-solid residue was obtained. On treating this with alkali and warming, little or nothing dissolved except ammonium chloride (absence of ethyl thioncarbanilate). The material had a strong odor of phenyl mustard oil, which was removed by treating with ether. On crystallizing from alcohol two substances were obtained, one melting at 150° (plates) which proved to be carbanilide, the other melting at 154° (prisms), which on analysis gave 18.2 per cent of nitrogen, while the calculated for monophenylthiourea is 18.4 per cent.

The phenylhydrazine salt of dithiophenylcarbazinic acid and ethylchlorcarbonate react in benzene solution without evolution

* Loc. cit.

of gas. On filtering from phenylhydrazine hydrochloride, evaporating the benzene solution, and then crystallizing the residue from a mixture of benzene and petroleum ether, colorless prisms were obtained which melted at 76°–77°. A nitrogen determination gave:

	Calculated for $C_6H_5NH—NHCO_2C_2H_5.H_2O$.	Found.
N.	14.1	14.5

The solution in sulphuric acid gave an intense red color with ferric chloride, the compound agreeing in properties with those described by Widman for ethyl phenylcarbazinate.

NEW HAVEN, May 14, 1900.

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